The effective sink strength of arrays of extended defects.

Talbot, D. R.S.

Award date:
1982

Awarding institution:
University of Bath


3 MAR 1982
PHD

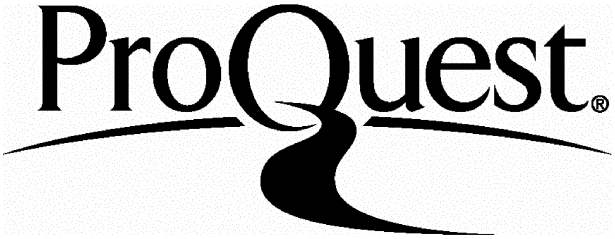
THE EFFECTIVE SINK STRENGTH OF ARRAYS OF EXTENDED DEFECTS

submitted by D.R.S. Talbot for the
degree of Ph.D. of the University of Bath.

1981

D Talbot.

D.R.S. Talbot



Abstract

In this dissertation we consider various schemes for estimating the effective sink strength of arrays of extended defects, in particular edge dislocations, loop dislocations and voids. Various approximate methods have been proposed in the past to deal with such arrays. We examine the relation between them for an array of edge dislocations and apply them to an array of loop dislocations. A feature of these approximations is their lack of sensitivity to the geometry of the array. We examine their limitations in this respect by considering a simple model problem for a random array of voids. We obtain a lower bound for the sink strength of the array which is extremely sensitive to its statistics. We display a distribution for which a simple self-consistent approximation violates the bound.

We give an alternative formulation of the model problem for a void array and generate a self-consistent scheme which allows for the distribution of voids. We demonstrate that a simple implementation of this scheme can also lead to results which still violate a lower bound but at a higher concentration than the simple self-consistent calculation.

We conclude that approximate methods should be used with caution at high concentrations of sinks.

Acknowledgements

I would like to thank Professor J.R. Willis and Dr. R. Bullough for their help and encouragement during the course of this work and gratefully acknowledge the support of the Science Research Council and the Atomic Energy Research Establishment, Harwell, through the tenure of an S.R.C. C.A.S.E. studentship.

CONTENTS

1. Introduction

An important problem associated with the operation of nuclear reactors, under both normal and abnormal conditions, is the prediction of the irradiation induced swelling of components, both fuel elements and structural components. A possible source of swelling lies in the formation of bubbles of fission gas which can act as sinks for any subsequently generated gas. In addition, the irradiation may 'damage' the material by causing displacement events so creating equal numbers of vacancies and interstitials (point defects) which rearrange themselves by diffusion. A review of the possible outcomes of this diffusion process has been given recently by Bullough and Hayns (1978). Briefly, a defect can be absorbed by any of the existing sinks in the material : gas bubbles, voids, dislocations and grain boundaries. It can also nucleate extended defects such as dislocation loops and voids. A vacancy-interstitial pair can annihilate itself by mutual recombination; in addition a defect can be trapped on a precipitate surface with an increased probability of recombining there. Certain of the sinks, namely dislocations, have a long range drift field associated with them. This field is stronger for interstitials than for vacancies and so causes a greater loss of interstitials than vacancies to the dislocations. The excess of vacancies is absorbed by relatively neutral sinks such as voids and this is thought to cause the swelling of the material.

The detailed modelling of these processes is a formidable task requiring, in general, the solution of a set of coupled non-linear diffusion equations in the presence of a microstructure whose evolution in time is to be found as part of the solution. The problem has some features in common with the description of chemical reactions and it is usual to apply to it a simplifying approximation known as 'chemical rate theory'. This has been applied to the radiation damage problem by, among others, Harkness and Li (1971), Brailsford and Bullough (1972) and Bullough and Hayns (1978). In this method, at any given instant, the microstructure is modelled by an effective medium containing continuous distributions of sinks of each type known to exist in the actual material. For each sink type, the continuous distribution is assumed to have a sink strength equal to the strength of the discrete array of sinks in the real material.

Then, assuming that the sink strengths are known, the flux of defects into each type of sink is determined from the diffusion equation for the effective medium. This, in turn, determines the excess flux of vacancies into the voids and hence determines the void swelling rate.

This then provides our motivation for discussing the sink strengths of arrays of sinks : if we leave aside the question of whether the microstructure can be successfully modelled by an effective medium, the more reliable our estimates for the sink strengths are, the more reliable predictions of void swelling based on them will be. In all that follows, unless explicitly stated to the contrary, we will make two simplifying assumptions : first, we assume steady state growth so that all parameters affecting the sink strengths are time-independent and second, we assume that the dimensions of the sinks are constant.

In the past, various approximate schemes for calculating the sink strengths have been proposed. A difficulty that is immediately encountered is that the sink strength of an array of extended defects of one type is not independent of the presence of other sinks. Mathematically, this is a severe problem, as any attempt to allow quantitatively for the presence of sinks of one type in an array of sinks of another type would, in general, lead to such a mixture of geometries as to make the problem intractable. In practice, it is usual to allow for the presence of other sinks by assuming they can be modelled by a continuous distribution of point sinks. Another difficulty concerns modelling the actual distribution of sinks. In practice they may be distributed randomly (in some sense) throughout the microstructure or, in the case of voids, they may be arranged on a lattice. Any scheme for estimating sink strengths should, therefore, make some allowance for the geometry of the array, even if it is only qualitative. We will return to this point later.

The simplest model so far proposed is the so called cell model. In this, the sinks (of one type only) are treated by considering a single sink situated in a cell, whose size is adjusted to obtain the volume concentration of sinks required, throughout which defects are generated at a constant rate K. The shape of the cell is usually taken to be the most convenient for the geometry of the sink. No flux of defects is allowed across the outer boundary of

the cell and appropriate conditions are applied on the sink boundary. The average concentration of defects within the cell, $\bar{c}$, is then calculated from the diffusion equation. If we assume that $\bar{c}$ is the average concentration of defects in the effective medium, the sink strength k^2 of the array follows by equating the generation rate K to the loss rate in the effective medium, $\hat{D}k^2\bar{c}$, where $\hat{D}$ is some overall diffusivity. This approach was used by Bullough et al (1981) to determine the sink strength of an array of dislocation loops. The approach was adopted earlier by Bullough and Perrin (1971) to determine void sink strengths in the presence of dislocations. For this problem, they modelled the effect of dislocation sinks by a distribution of point sinks within the cell. A variant of this cell model was proposed, in the context of edge dislocation sinks, by Heald and Speight (1975). Instead of defects being generated throughout the cell, they imposed a constant concentration condition on the cell boundary. The Heald-Speight model was discussed in some detail by Brailsford and Bullough (1976) and we return to it in chapter 2.

Another approach has its origins in work of Maxwell (1892) on the electrical resistivity of a two phase composite; it has been developed over the years by many authors, amongst whom it is perhaps appropriate to mention Kerner(1956) and Brailsford and Major (1964).

In the present context, for a material containing only randomly distributed voids, the idea is to construct the effective medium in the following way : we embed a void of radius a surrounded by a spherical shell of sink free material of outer radius R in the effective medium, in such a way that the overall sink strength of this composite is the same as that of the effective medium. To do this we require that a^3/R^3 be equal to the volume concentration of voids in the material. This scheme provides a self-consistent method for calculating the overall sink strength of the array. It was applied in an extended form by Brailsford and Bullough (1972) and by Brailsford, Bullough and Hayns (1976) to an array of voids with other sinks present. Brailsford et al. (1976) also considered the effect of setting R = a, that is, embedding a void directly in the effective medium. This approach was used by Bullough and

Hayns (1978) and is analogous to a calculation of Brinkman (1947), which applied to viscous flow past a fixed set of obstacles. We will consider its validity in chapter 4.

When the sinks are dislocations the problem is complicated by the presence of an energy of interaction between the defects and the dislocation. Apart from the Heald-Speight model, another approach is the "pseudo-effective medium" method of Brailsford and Bullough (1976). This is a derivative of the above method in that it employs a sink free zone whose radius is now related to the characteristic length of the interaction energy as well as the dislocation density. We will describe this model in chapter 2.

The above methods (cell models and self-consistent schemes) make no explicit allowance for the actual distribution of sinks in the real material. If they make any allowance at all, it is only qualitative in the sense that the presence of other sinks is modelled by continuous distributions rather than by discrete sinks. Brailsford (1976) considered a model problem of diffusion to a random array of voids and allowed explicitly for the statistics of the array. For low void concentrations, he used perturbation theory to verify the self-consistent estimate obtained by embedding one void directly in the effective medium. He also obtained higher order corrections to the sink strength, again valid only at low concentrations.

The purpose of this work is twofold : in the next two chapters we compare the estimates obtained using the simple models described above for two different sink types, namely, straight and loop dislocations. The models are convenient in that they provide simple estimates for overall sink strengths at any concentration of sinks, but these estimates do not all agree at higher concentrations. Thus some judgement is needed in choosing the most appropriate model (the self consistent calculations are usually preferred). As a contribution towards making this judgement, in the final two chapters we consider more rigorously than any of the simple methods allow, the problem of estimating sink strengths at finite concentrations. In these chapters we will only treat void sink strengths.

In chapter 2 we analyse the problem of diffusion to straight edge dislocations. We assume that the dislocation core is an infinitely long circular cylinder so that the problem is effectively two-dimensional. We describe a self-consistent scheme, with which we compare the models of Heald and Speight (1975) and, Brailsford and Bullough (1976). The analysis is complicated by the interaction between the dislocation and the defects and also by the possibility of using a "rate control" boundary condition on the dislocation core. The alternative core boundary condition is that the defect concentration be zero there : the so called 'perfect' sink condition. In the limit of low dislocation densities we show that for the Heald-Speight model these two conditions give the same result in the range of parameter values of interest to Brailsford and Bullough (1976). Consequently we use the simpler perfect sink condition during the analysis of the self-consistent scheme, for which we use the method of matched asymptotic expansions. Our comparison of the three methods shows that in the low density limit they give the same result. However, owing to the systematic nature of the method of solution we prefer the self-consistent scheme.

In chapter 3 we treat the problem of diffusion to loop dislocations. Here we assume that the dislocation core is toroidal. We use both of the cell models described above as well as a self-consistent scheme. In each case, we analyse the problem for neutral loops and for loops having an energy of interaction with the defects. If the defects are vacancies, it is reasonable to assume that the loops have no drift field associated with them. The complicated geometry allows us only to obtain approximate results under certain conditions which we discuss later. Nevertheless, we show that in the limit of low loop densities the results obtained using the self-consistent scheme are consistent with those obtained using cell models.

In neither of these chapters do we assume there is more than one population of sinks or one population of defects. Our main aim is to compare different methods of modelling arrays of sinks at low densities rather than to obtain results pertinent to the swelling problem. The extension to include qualitatively the effects of other sinks (via continuous distributions) involves no question of principle, but increases the complexity of the algebra considerably.

In chapter 4 we assess the validity of a simple self-consistent scheme for calculating the sink strength of an array of voids. We do this through a detailed study of a simple model problem, which involves a random distribution of identical spherical voids acting as sinks for just one diffusing population of defects. The steady-state diffusion problem we consider can be characterized by a variational principle which we use to obtain lower bounds on the sink strength of the array. The statistics of the array are incorporated by extremizing the expectation value of the variational functional with respect to configuration-dependent trial fields. We thus obtain bounds for the sink strength involving correlations between voids. These bounds are extremely sensitive to the statistics of the array; if we use the so called 'well-stirred' approximation an apparent lower bound actually becomes infinite at a finite concentration. This leads us to believe that this approximation is inconceivable as the result of any stochastic mixing process at high concentrations. Clearly, postulated pair correlation functions must satisfy some set of conditions (of which finiteness of our bound is an example) but a complete set of necessary and sufficient conditions is at present unknown. Reassuringly, if we use the distributions obtained from the stochastic models of Matern (1960) and from the approximation of Percus and Yevick (1957) for a statistical mechanical distribution of hard spheres, the bounds we obtain are well behaved. In the limit of low concentrations, these distributions reduce to the well-stirred approximation; it is in this limit that the approximation has been used by Batchelor and Green (1972), Willis and Acton (1976) and others.

The self-consistent estimate is not sensitive to the statistics of the array and we display pair correlation functions for which the rigorous lower bound exceeds the estimate at high concentrations of voids. This is in contrast to the situation when overall elastic moduli are calculated, for which the usual self-consistent estimates always lie between the Hashin-Shtrikman bounds (see, for example, Kroner (1977) or Willis (1977)), We conclude, therefore, that care should be exercised in using the self-consistent estimate except at low concentrations. At higher concentrations it would seem preferable to use our bound even with some approximate pair distribution function.

We also demonstrate a solution to the problem based on perturbation theory and relate it to the results obtained from the variational principle. We remark that the problem is analogous to that of finding the viscous drag exerted by an array of spherical obstacles. The perturbation theory we use is closely related to that developed by Childress (1972) and Hinch (1977) for example, and the self-consistent calculation is analogous to one performed by Brinkman (1947).

In the final chapter, we obtain self-consistent estimates for the sink strength of an array of voids which allow for correlations between voids. We consider a more general composite consisting of spheres of lossy material of one type embedded in a matrix of lossy material of a second type. Then, in the limit of the sink strength of the 'void' material becoming infinite and the sink strength of the matrix material becoming zero, we recover the problem discussed in chapter 4. For this lossy composite we define a 'polarization concentration', which is directly analogous to the momentum polarization introduced by Willis (1980), using a homogeneous lossy comparison medium. We reformulate the problem as a variational principle in a manner closely related to work of Willis (1981a). This principle does not, in general, furnish us with bounds, but rather provides a systematic way of generating approximate solutions without recourse to the type of closure assumptions associated with perturbation theory. We again optimize the expectation value of the variational functional with respect to simple configuration-dependent trial fields to obtain results capable of giving estimates of the overall sink strength which depend on the comparison material. However, if we choose the comparison material to have the properties of the effective medium, we obtain an implicit equation for the sink strength of the effective medium which depends on pairwise correlations between voids. If we compare the results we get using this procedure and the Percus-Yevick approximation with those of chapter 4, we find that although they exceed the simple self-consistent estimates they violate the lower bound at a concentration of about 1/3.

We developed the method of this chapter to treat the problem of diffusion to an array of parallel neutral edge dislocations. It would be desirable to have some idea of the validity of self-consistent estimates for this two-dimensional problem, even in the absence of drift fields. However, if we try to apply the analysis in chapter 4 directly, we are unable, at present, to obtain results independent of the shape and size of the region in which the dislocations are embedded. This difficulty arises because the Green function for Laplace's equation in two dimensions displays logarithmic growth at infinity and makes it impossible to obtain convergent integrals using the simple trial fields of chapter 4. Intuitively, however, a dislocation situated far from the outer boundary of the region and surrounded by many other dislocations might be expected to be screened from any boundary effects. The theory of chapter 5 embodies this screening through the use of a lossy comparison material and might be expected to provide better estimates of the effective sink strength than the simple self-consistent calculation. However, judging from the comparison with our lower bound for voids we would not expect the method to provide especially reliable results for arrays of dislocations at high concentrations. At the time of writing, realizable pair distribution functions for arrays of parallel cylinders are unknown to us. We hope, however, to report the extension to this case at a later date. Finally, we note that the theory in chapter 5 can be extended to include the effect of other sinks by regarding the matrix as a continuous distribution of these sinks.

The work contained in chapter 4 has been published jointly with J.R. Willis. A copy is bound into the rear of this thesis.

2. The Effective Sink Strength of an Array of Straight Dislocations

2.1 Introduction

In this chapter we discuss the problem of finding the effective sink strength, under steady state conditions of a random array of aligned straight dislocations to a diffusing population of point defects. In order to simplify the analysis we will only consider the diffusion of a single population of defects although it could be extended to cover the case of more than one.

The full problem of diffusion to a random array of dislocations admits no easy exact formulation. Instead we consider a self-consistent approximation similar to that used for finding the overall moduli of composite materials. We do not consider its validity here, but rather assume that it will hold in the limit of low concentrations when the interaction between dislocations will be small. We assume that the random array of discrete dislocations can be replaced by a continuous distribution of sinks forming a 'lossy' medium of strength k^2 so that, overall, the concentration c of defects satisfies

$$D\left(\nabla^2 c - k^2 c\right) + K' = 0, \qquad (2.1.1)$$

where D is the overall diffusivity and K' is the rate of generation of defects. We will estimate k^2 self-consistently in terms of the dislocation density ρ_D by embedding one dislocation into the lossy medium. We then equate the total flux of defects per unit length into this dislocation to $k^2 \bar{c} D/\rho_D \Omega$, where $\bar{c}$ is the concentration far from the dislocation and Ω is the atomic volume and solve the resulting equation for k^2.

We therefore have to solve

$$\underline{\nabla}.\underline{J} - Dk^2 c + K' = 0, \qquad (2.1.2)$$

where $-\underline{J}$ is the flux of defects, so that

$$\underline{J} = \left(D\underline{\nabla}c + \frac{D}{E'} c \underline{\nabla} E\right), \qquad (2.1.3)$$

E' being the thermal energy and E the interaction energy between the point defect and the dislocation, subject to suitable boundary conditions.

In this chapter we will consider two core boundary conditions, namely

$$C = 0, \quad r = r_0, \tag{2.1.4}$$

and

$$\underline{J} \cdot \underline{n} = D\alpha C, \quad r = r_0, \tag{2.1.5}$$

where r is the radial distance from the centre of the dislocation, r_0 is the radius of the dislocation core, $\underline{n}$ is the unit normal out of the dislocation and α is a parameter related to the transfer velocity of defects across the matrix sink interface. This "rate control" boundary condition is that used by Brailsford and Bullough (1976). We note that (2.1.4) is recoverable from (2.1.5) in the limit $\alpha \to \infty$. We do not attempt to solve (2.1.2) exactly, but instead consider two approximate methods of solution : the 'pseudo-effective medium' approach of Brailsford and Bullough (1976) and that of matched asymptotic expansions.

For completeness in section 2.2 we will also describe the cell model due to Heald and Speight although the spirit of their approach differs from that of the self-consistent approximation. They consider one dislocation surrounded by a sink free zone of radius R where R is half the separation between neighbouring sinks, and, where, implicit in the definition of R is the assumption that the dislocations are arranged on a lattice. With this assumption of a lattice, for low dislocation densities R is approximately $(\pi \rho_D)^{-1/2}$. The production of defects in the cell is simulated by a constant concentration boundary condition on the outer surface r = R.

We consider the Heald-Speight model for two cases: first, when the core boundary condition is given by (2.1.4) and second when it is given by 2.1.5. The solution in the latter case was given by Brailsford and Bullough (1976). We discuss its range of validity and show that, for the range of parameters they consider, the effect of rate limitation at the core boundary is small. Bearing this in mind, when we discuss the pseudo-effective medium approach in section 2.3 and our self-consistent scheme in 2.4, we will only use the core condition (2.1.4).

2.2 The Heald-Speight Model

Heald and Speight consider one dislocation surrounded by a sink free zone of radius $R = (\pi \rho_D)^{-1/2}$ and simulate the production of defects within the zone by a constant concentration boundary condition on R, namely

$$c = \bar{c}. \tag{2.2.1}$$

The steady state concentration in the region $r_0 \leq r \leq R$ is given by the solution of

$$\underline{\nabla} . \underline{J} = 0. \tag{2.2.2}$$

In the absence of any externally applied stress, a point defect with coordinates (r, θ) centred on the axis of a straight dislocation has an interaction energy per unit length given by (see, for example, Bullough and Newman (1970))

$$E = \frac{\mu b}{\pi} V e \frac{\sin\theta}{r}, \tag{2.2.3}$$

where e is the relaxation volume strain associated with the isolated point defect, and V is the volume of the effective spherical elastic inclusion representing the point defect. For convenience we will write

$$\frac{E}{E'} = \frac{L \sin\theta}{r}, \tag{2.2.4}$$

where

$$L = \frac{\mu b V e}{\pi E'}. \tag{2.2.5}$$

We now introduce the change of variable given by Margvelashvili and Saralidze (1974)

$$C(r,\theta) = Z(r,\theta)\, e^{-\frac{1}{2}E/E'}, \tag{2.2.6}$$

which, remembering that E/E' is harmonic, transforms (2.2.2) into

$$\nabla^2 Z - \frac{L^2}{4r^4} Z = 0. \tag{2.2.7}$$

This equation has general solution

$$\bar{z}(r,\theta) = \sum_{n=0}^{\infty}{}' \left(A_n \bar{I}_n\left(\tfrac{L}{2r}\right) + B_n K_n\left(\tfrac{L}{2r}\right)\right) \cos n\theta, \tag{2.2.8}$$

where I_n, K_n are modified Bessel functions. Now if $L/2R \ll 1$, on $r = R$ $Z \sim \bar{c}$, so applying this condition and $c(r_0) = 0$ we find that the only non-zero A_n or B_n are

$$A_0 = \bar{c}\, K_0\left(\tfrac{L}{2r_0}\right)\left[\bar{I}_0\left(\tfrac{L}{2R}\right) K_0\left(\tfrac{L}{2r_0}\right) - K_0\left(\tfrac{L}{2R}\right) \bar{I}_0\left(\tfrac{L}{2r_0}\right)\right]^{-1}, \tag{2.2.9}$$

and

$$B_0 = -\bar{c}\, \bar{I}_0\left(\tfrac{L}{2r_0}\right)\left[\bar{I}_0\left(\tfrac{L}{2R}\right) K_0\left(\tfrac{L}{2r_0}\right) - K_0\left(\tfrac{L}{2R}\right) \bar{I}_0\left(\tfrac{L}{2r_0}\right)\right]^{-1}. \tag{2.2.10}$$

Hence the radial component of the flux into the dislocation is

$$J_r(r_0,\theta) = -\frac{D}{r_0}\, e^{-\frac{L\sin\theta}{2r_0}}\, \frac{\bar{c}}{\bar{I}_0\left(\tfrac{L}{2R}\right) K_0\left(\tfrac{L}{2r_0}\right) - K_0\left(\tfrac{L}{2R}\right) \bar{I}_0\left(\tfrac{L}{2r_0}\right)}, \tag{2.2.11}$$

and so the total flux per unit length into the dislocation, F, is given by

$$F = -\frac{1}{\Omega}\int_0^{2\pi} \underline{n}\cdot\underline{J}\, d\theta$$

$$= \frac{2\pi D \bar{c}\, \bar{I}_0\left(\tfrac{L}{2r_0}\right)}{\Omega\left[K_0\left(\tfrac{L}{2R}\right)\bar{I}_0\left(\tfrac{L}{2r_0}\right) - \bar{I}_0\left(\tfrac{L}{2R}\right) K_0\left(\tfrac{L}{2r_0}\right)\right]}. \tag{2.2.12}$$

Hence the overall sink strength of the array is given by

$$\frac{K^2}{\ell_D} = \frac{2\pi\, \bar{I}_0\left(\tfrac{L}{2r_0}\right)}{\left[K_0\left(\tfrac{L}{2R}\right)\bar{I}_0\left(\tfrac{L}{2r_0}\right) - \bar{I}_0\left(\tfrac{L}{2R}\right) K_0\left(\tfrac{L}{2r_0}\right)\right]}. \tag{2.2.13}$$

An exact analytic solution of (2.2.7) subject to the core boundary condition

$$\underline{J}.\underline{n} = D\alpha c, \tag{2.2.14}$$

is not available but an approximate solution was given by Brailsford and Bullough (1976). However, as was mentioned in the introduction, we shall see that its validity is limited.

With the change of variables (2.2.6), (2.2.14) becomes

$$\frac{\partial Z}{\partial r} - \frac{L\sin\theta}{2r^2} Z - \alpha Z = 0, \quad r = r_0, \tag{2.2.15}$$

and, with the further changes of variables

$$z = L/2r, \tag{2.2.16}$$

and

$$\phi = \frac{\pi}{2} - \theta, \tag{2.2.17}$$

(2.2.15) becomes

$$\frac{\partial Z}{\partial z} + (\beta + \cos\phi) Z = 0, \quad z = z_0, \tag{2.2.18}$$

where

$$\beta = \frac{2r_0^2}{L}\alpha. \tag{2.2.19}$$

The other boundary condition (2.2.1) becomes, with $z_R = L/2R$,

$$Z(z_R, \phi) = \bar{c}\, e^{z_R \cos\phi}. \tag{2.2.20}$$

The general solution of (12) in these variables is

$$Z(z,\phi) = \sum_{n=0}^{\infty}{}' \left(A_n I_n(z) + B_n K_n(z)\right) \cos n\phi, \tag{2.2.21}$$

the solutions involving $\sin(n\phi)$ having been rejected because they have the wrong symmetry.

Applying the boundary condition (2.2.20),

$$A_n \bar{I}_n(z_R) + B_n K_n(z_R) = \bar{c}\, \bar{I}_n(z_R), \tag{2.2.22}$$

and applying (2.2.18) we find

$$A_0 \left(\bar{I}_0'(z_0) + \beta \bar{I}_0(z_0)\right) + \tfrac{1}{2} A_1 \bar{I}_1(z_0) + B_0 \left(K_0'(z_0) + \beta K_0(z_0)\right) + \tfrac{1}{2} B_1 K_1(z_0) = 0, \tag{2.2.23}$$

$$A_1 \left(\bar{I}_1'(z_0) + \beta \bar{I}_1(z_0)\right) + A_0 \bar{I}_0(z_0) + \tfrac{1}{2} A_2 \bar{I}_2(z_0) + B_1 \left(K_1'(z_0) + \beta K_1(z_0)\right) + B_0 K_0(z_0) + \tfrac{1}{2} B_2 K_2(z_0) = 0, \tag{2.2.24}$$

and in general ($n \geq 2$)

$$A_n \left(\bar{I}_n'(z_0) + \beta \bar{I}_n(z_0)\right) + \tfrac{1}{2}\left(A_{n+1} \bar{I}_{n+1}(z_0) + A_{n-1} \bar{I}_{n-1}(z_0)\right) + B_n \left(K_n'(z_0) + \beta K_n(z_0)\right) + \tfrac{1}{2}\left(B_{n+1} K_{n+1}(z_0) + B_{n-1} K_{n-1}(z_0)\right) = 0. \tag{2.2.25}$$

Brailsford and Bullough (1976) now argue that, with $z_0 = L/2r_0 \gg 1$, $I_n(z_0)$, $K_n(z_0)$, $I_n'(z_0)$ and $K_n'(z_0)$ can be replaced by their large argument expansions; however, these expansions are only valid if $z_0 > n$ and as eventually $n > z_0$ some care is needed in using these approximations. We first assume that $z_R \ll 1$ (low dislocation density) and so we can replace (2.2.22) by

$$A_0 \bar{I}_0(z_R) + B_0 K_0(z_R) = \bar{c}, \tag{2.2.26}$$

$$A_n \bar{I}_n(z_R) + B_n K_n(z_R) = 0. \tag{2.2.27}$$

We now assume that we can solve (2.2.23) to (2.2.27) for the A_n and B_n and that the series (2.2.21) is convergent for all z with these values of A_n and B_n. We note that, because we are using (2.2.26) and (2.2.27) instead of (2.2.22), the series obtained will, even before truncation, only be an approximation to the true Z.

Now the large argument expansions for I_n, I_n', K_n and K_n' give

$$I_n'(z_0) \simeq I_n(z_0) \simeq \frac{e^{z_0}}{\sqrt{2\pi z_0}} = I(z_0), \tag{2.2.28}$$

and

$$K_n'(z_0) \simeq -K_n(z_0) \simeq e^{-z_0}\sqrt{\frac{\pi}{2z_0}} = K(z_0), \tag{2.2.29}$$

so long as $n \lesssim N$, where N is of the order of z_0. Using these in (2.2.23) to (2.2.25) we find

$$A_0(1+\beta) + \tfrac{1}{2}A_1 + \frac{1}{\varepsilon}B_0(\beta-1) = 0, \tag{2.2.30}$$

$$A_0 + A_1(1+\beta) + \tfrac{1}{2}A_2 + \frac{1}{\varepsilon}B_0 = 0, \tag{2.2.31}$$

and

$$A_n(1+\beta) + \tfrac{1}{2}(A_{n+1} + A_{n-1}) = 0, \tag{2.2.32}$$

where

$$\varepsilon = I(z_0)/K(z_0). \tag{2.2.33}$$

A solution of (2.2.32) that is appropriate so long as N is reasonably large is

$$A_n = A_1 q^{n-1}, \tag{2.2.34}$$

where

$$q = -(\beta+1) + \left((\beta+1)^2 - 1\right)^{1/2}, \tag{2.2.35}$$

and we have chosen the positive value of the root to ensure that $|q|<1$ for all $\beta>0$. Substituting (2.2.34) in (2.2.31) and solving the remaining equations (2.2.26), (2.2.27) and (2.2.30) we get

$$A_0 \simeq \tfrac{1}{2}A_1\left[(\beta-1)(1+\beta+\tfrac{1}{2}q) - \tfrac{1}{2}\right], \tag{2.2.36}$$

$$B_0 \simeq -\tfrac{1}{2}\varepsilon A_1\left[(\beta+1)(1+\beta+\tfrac{1}{2}q) - \tfrac{1}{2}\right], \tag{2.2.37}$$

$$A_1 \simeq 2\bar{c}\left\{\left[(\beta-1)(1+\beta+\tfrac{1}{2}q) - \tfrac{1}{2}\right] I_0(z_R)\right\}^{-1}. \tag{2.2.38}$$

Brailsford and Bullough are interested in the limit $\beta \to 0$ which implies $q \simeq -1 + \sqrt{2\beta}$. Using this value of q,

$$A_0 \simeq \frac{\bar{c}\,(1-\sqrt{\frac{\beta}{2}})}{I_0(z_R) + \varepsilon\sqrt{\frac{\beta}{2}}\,K_0(z_R)}\,, \tag{2.2.39}$$

$$B_0 \simeq \frac{\bar{c}\,\varepsilon\sqrt{\frac{\beta}{2}}}{I_0(z_R) + \varepsilon\sqrt{\frac{\beta}{2}}\,K_0(z_R)}\,, \tag{2.2.40}$$

$$A_1 \simeq \frac{-2\bar{c}}{I_0(z_R) + \varepsilon\sqrt{\frac{\beta}{2}}\,K_0(z_R)}\,, \tag{2.2.41}$$

$$A_n \simeq A_1(-1)^{n-1}\left(1-(n-1)\sqrt{\frac{\beta}{2}}\right), \tag{2.2.42}$$

$$B_n \simeq -A_n\, I_n(z_R)/K_n(z_R). \tag{2.2.43}$$

The rate of introduction of defects through the surface r = R, and hence the loss rate of defects into the dislocation, has the general form

$$F \simeq -\frac{DL\pi}{R\Omega}\sum_{n=0}^{\infty}(-1)^n I_n(z_R)\left\{A_n I_n'(z_R) + B_n K_n'(z_R)\right\}. \tag{2.2.44}$$

Now for in$n \lesssim N$, A_n and B_n are given approximately by (2.2.42) and (2.2.43), which show that successive terms in (2.2.44) decrease rapidly since z_R is small. Truncating this series after one term, therefore, we find

$$F \simeq \frac{2\pi D\bar{c}}{\Omega}\cdot\frac{\varepsilon\sqrt{\frac{\beta}{2}}}{I_0(z_R) + \varepsilon\sqrt{\frac{\beta}{2}}\,K_0(z_R)}\,. \tag{2.2.45}$$

Hence,

$$\frac{\kappa^2}{\beta_D} \simeq \frac{2\pi\varepsilon\sqrt{\frac{\beta}{2}}}{I_0(z_R) + \varepsilon\sqrt{\frac{\beta}{2}}\,K_0(z_R)} . \qquad (2.2.46)$$

Noting that $I_0(z_R) \simeq 1$ and that $\varepsilon, K_0(z_R) \gg 1$ we find

$$\frac{\kappa^2}{\beta_D} \simeq \frac{2\pi}{K_0(z_R)} , \qquad (2.2.47)$$

and if we use the same approximations in (2.2.13) we find that it too reduces to (2.2.47). We conclude, therefore, that at low dislocation densities the effect of rate limitation at the core boundary is unimportant, so long as the parameter β is small. In fact, if α is finite and yet β is small, the term involving $\frac{L\sin\theta}{2r_0^2}Z$ in the boundary condition (2.2.15) is the dominant one, and so forces (2.2.15) to reduce approximately to $Z = 0$. The novelty of Brailsford and Bullough's approximation is that it demonstrates this explicitly and also could be used at finite β. We emphasise, however that their approximation depends on z_0 being greater than N and so it is not possible to generate a series such as (2.2.44) which approximates F to arbitrary accuracy.

2.3 The Pseudo-Effective Medium Approach

If we use the change of variables (2.2.6) in (2.1.2) we find

$$\nabla^2 Z - \left(\frac{L^2}{4r^4} + \kappa^2\right) Z + K e^{\frac{L\sin\theta}{2r}} = 0, \qquad (2.3.1)$$

where we have written, for convenience,

$$K = \frac{K'}{D} . \qquad (2.3.2)$$

Also, from the outer boundary condition $c \to \bar{c}$ as $r \to \infty$,

$$K = \kappa^2 \bar{c} . \qquad (2.3.3)$$

By considering the term involving Z in (2.3.1) and observing that when $r \gg \left(\frac{L}{2\kappa}\right)^{1/2}$ $L^2/4r^4 \ll \kappa^2$, Brailsford and Bullough propose that the dislocation be surrounded by a sink free zone of radius r_c where

$$r_c = \left(\frac{L}{2\kappa}\right)^{1/2} . \qquad (2.3.4$$

Thus we are led to consider the system of equations

$$\nabla^2 Z - \frac{L^2}{4r^4} Z + \kappa^2 \bar{c}\, e^{\frac{L\sin\theta}{2r}} = 0, \quad r \le r_c, \tag{2.3.5}$$

$$\nabla^2 c - \kappa^2 c + \kappa^2 \bar{c} = 0, \quad r \ge r_c, \tag{2.3.6}$$

where, in addition to a core boundary condition, c and $\partial c/\partial r$ are taken to be continuous on $r = r_c$. These equations are not easily soluble due to the θ dependence in the last term of (2.3.5) but, we only consider small values of k^2 and correspondingly ignore this term. A further source of difficulty is the continuity condition on $\partial c/\partial r$ on $r = r_c$. However, if we take $L/2r_c \ll 1$, we can replace this by the simpler condition that $\partial Z/\partial r$ be continuous there. Regarding the core boundary condition to be used, following our comments at the end of section 2.2 we only consider

$$c = 0, \quad r = r_0. \tag{2.3.7}$$

The general solution of (2.3.6) is

$$c = \bar{c} + \sum_{n=0}^{\infty} C_n K_n(\kappa r) \cos n\theta, \tag{2.3.8}$$

and of (2.3.5) without the last term is

$$Z = \sum_{n=0}^{\infty}{}' \left[A_n I_n\left(\frac{L}{2r}\right) + B_n K_n\left(\frac{L}{2r}\right) \right] \cos n\theta. \tag{2.3.9}$$

We now apply the boundary (2.3.7) and the continuity conditions on Z on $r = r_c$ to find, when $r \le r_c$

$$Z = A \left[I_0\left(\frac{L}{2r_0}\right) K_0\left(\frac{L}{2r}\right) - K_0\left(\frac{L}{2r_0}\right) I_0\left(\frac{L}{2r}\right) \right], \tag{2.3.10}$$

where

$$A = \bar{c} \left\{ 2 I_0\left(\frac{L}{2r_0}\right) K_0(\kappa r_c) - I_0\left(\frac{L}{2r_0}\right) I_0(\kappa r_c) - \frac{K_0\left(\frac{L}{2r_0}\right) I_0'(\kappa r_c)\, K_0(\kappa r_c)}{K_0'(\kappa r_c)} \right\}^{-1}. \tag{2.3.11}$$

We only need the radially symmetric solution because, when $L/2r_c \ll 1$, $e^{-L/2r\cos\theta} \sim 1$ for $r \gtrsim r_c$. Hence, the total flux into the dislocation is given by

$$F = A\,\frac{2\pi D}{\Omega}\,I_0(L/2r_0)\,. \tag{2.3.12}$$

From (2.3.4), $kr_c = \left(\frac{\kappa L}{2}\right)^{1/2}$ and so when $kL \ll 1$

$$A \simeq \frac{\bar{c}}{2\,I_0\left(\frac{L}{2r_0}\right)K_0(\kappa r_c)}\,, \tag{2.3.13}$$

and the (implicit) equation for k^2 is given by

$$\frac{\kappa^2}{f_D} = \frac{\pi L}{K_0(\kappa r_c)}\,. \tag{2.3.14}$$

With the initial approximation $k \sim (\pi f_D)^{1/2}$, this becomes

$$\frac{\kappa^2}{f_D} \simeq \frac{\pi L}{K_0\left(r_c(\pi f_D)^{1/2}\right)}\,, \tag{2.3.15}$$

and, on using the small argument expansion of K_0 we find

$$\frac{\kappa^2}{f_D} \simeq \frac{2\pi L}{\ln\left(8/L(\pi f_D)^{1/2}\right) - 2\gamma}\,, \tag{2.3.16}$$

where γ is Euler's constant. Using the same expansion in (2.2.13) for comparison, we get

$$\frac{\kappa^2}{f_D} \simeq \frac{2\pi L}{\ln\left(4/L(\pi f_D)^{1/2}\right) - \gamma}\,, \tag{2.3.17}$$

which to lowest order in f_D is the same as (2.3.16).

2.4 Solution by Matched Asymptotic Expansions

We revert to the full equation transformed by (2.2.6)

$$\nabla^2 Z - \frac{L^2}{4r^4}Z - \kappa^2 Z + \kappa^2 \bar{c}\, e^{\frac{L\sin\theta}{2r}} = 0\,, \tag{2.4.1}$$

together with

$$Z = 0\,, \quad r = r_0\,, \tag{2.4.2}$$

$$Z \to \kappa^2 \bar{c}\,, \quad r \to \infty\,. \tag{2.4.3}$$

We will consider the solution to (2.4.1) in the limit of small k. This is a reasonable assumption to make, for,

$$\frac{Dk^2}{\Omega} = F f_D , \tag{2.4.4}$$

where F is the loss rate into the dislocation (which depends on k). Clearly, as $f_D \to 0$ $k \to 0$ and, as we mentioned in the introduction, it is only in this limit that we expect (2.4.1) and (2.4.4) to provide a good approximation to the overall sink strength of the array.

Now, if k is small (2.4.1) can be solved iteratively. The first approximation is obtained from

$$\nabla^2 Z - \frac{L^2}{4r^4} Z = 0 ; \tag{2.4.5}$$

a solution dependent on r only is

$$Z = A K_0\left(\frac{L}{2r}\right) + B I_0\left(\frac{L}{2r}\right). \tag{2.4.6}$$

Applying the inner boundary condition this becomes

$$Z = A\left(K_0\left(\frac{L}{2r}\right) I_0\left(\frac{L}{2r_0}\right) - I_0\left(\frac{L}{2r}\right) K_0\left(\frac{L}{2r_0}\right)\right), \tag{2.4.7}$$

for some A.

Note, however, that, as $r \to \infty$, $K_0 \sim \ln\left(\frac{L}{2r}\right)$ and so (2.4.7) cannot satisfy the outer boundary condition. In fact, as $r \to \infty$ (2.4.5) is not a good approximation to (2.4.2), for $L^2/4r^4 \to 0$ and $e^{L\sin\theta/2r} \to 1$.

Formally we define a new 'stretched' variable

$$R = kr, \tag{2.4.8}$$

in terms of which (2.4.1) becomes

$$k^2\left(\frac{\partial^2 Z}{\partial R^2} + \frac{1}{R}\frac{\partial Z}{\partial R} + \frac{1}{R^2}\frac{\partial^2 Z}{\partial \theta^2}\right) - \frac{k^4 L^4}{4R^4} Z$$

$$- k^2 Z + k^2 \bar{c}\, e^{\frac{kL\sin\theta}{2R}} = 0, \tag{2.4.9}$$

that is,

$$\frac{\partial^2 Z}{\partial R^2} + \frac{1}{R}\frac{\partial Z}{\partial R} + \frac{1}{R^2}\frac{\partial^2 Z}{\partial \theta^2} - Z + \bar{c} = \frac{\kappa^2 L^2 Z}{4R^4} + \left(1 - e^{\frac{\kappa L \sin\theta}{2R}}\right)\bar{c}. \tag{2.4.10}$$

If we let $k \to 0$ and keep R fixed, so that r becomes large, (2.4.10) becomes, asymptotically,

$$\frac{\partial^2 Z}{\partial R^2} + \frac{1}{R}\frac{\partial Z}{\partial R} + \frac{1}{R^2}\frac{\partial^2 Z}{\partial \theta^2} - Z + \bar{c} = 0, \tag{2.4.11}$$

which has a solution dependent on r only:

$$Z = \bar{c} + C K_0(R). \tag{2.4.12}$$

This satisfies the condition $Z \to \bar{c}$ as $R \to \infty$, since $K_0(R) \sim R^{-1/2} e^{-R}$ as $R \to \infty$. We must now find the constants A and C. This is done by invoking the matching principle of Van Dyke (1964), that the m-term outer expansion of the n-term inner expansion equals the n-term inner expansion of the m-term outer expansion. Since (2.4.7) and (2.4.12) are one-term expansions it follows that here, m=n= 1.

To follow the prescription we write (2.4.7) in terms of the outer variable R and expand to zeroth order in k, ln k counting as O(1). Thus.

$$Z \sim A\left\{\left[-\ln\left(\frac{\kappa L}{4R}\right) - \gamma\right] I_0\left(\frac{L}{2r_0}\right) - K_0\left(\frac{L}{2r_0}\right)\right\}. \tag{2.4.13}$$

Dually, we write R in terms of r in (2.4.12) and expand to get

$$Z \sim \bar{c} - C\left(\ln\left(\frac{R}{2}\right) + \gamma\right). \tag{2.4.14}$$

The right hand sides of (2.4.13), (2.4.14) should agree identically; therefore, equating coefficients in $\ln(R)$

$$A I_0\left(\frac{L}{2r_0}\right) = -C, \tag{2.4.15}$$

and for the constants to agree

$$A\left\{\left[-\ln\left(\frac{\kappa L}{4}\right) - \gamma\right] I_0\left(\frac{L}{2r_0}\right) - K_0\left(\frac{L}{2r_0}\right)\right\} = \bar{c} - C\left(\ln\frac{1}{2} + \gamma\right). \tag{2.4.16}$$

Solving (2.4.15) and (2.4.16) for A and C we get

$$A = -\bar{c}\left[\left(2\gamma+\ln\left(\frac{KL}{8}\right)\right)I_0\left(\frac{L}{2r_0}\right)+K_0\left(\frac{L}{2r_0}\right)\right]^{-1}, \tag{2.4.17}$$

and

$$C = \bar{c}\,I_0\left(\frac{L}{2r_0}\right)\left[\left(2\gamma+\ln\left(\frac{KL}{8}\right)\right)I_0\left(\frac{L}{2r_0}\right)+K_0\left(\frac{L}{2r_0}\right)\right]^{-1}. \tag{2.4.18}$$

Hence from (2.4.7) and (2.4.17) we find

$$F = \frac{D}{\Omega}\cdot\frac{-2\pi\bar{c}\,I_0(L/2r_0)}{\left(2\gamma+\ln\left(\frac{KL}{8}\right)\right)I_0\left(\frac{L}{2r_0}\right)+K_0\left(\frac{L}{2r_0}\right)}, \tag{2.4.19}$$

and so

$$\frac{K^2}{f_D} = \frac{2\pi\,I_0(L/2r_0)}{\left(\ln\frac{8}{KL}-2\gamma\right)I_0\left(\frac{L}{2r_0}\right)-K_0\left(\frac{L}{2r_0}\right)}. \tag{2.4.20}$$

Furthermore, if we assume that $L/2r_0 \gg 1$, (2.4.20) becomes, on using the large argument expansion of K_0,

$$\frac{K^2}{f_D} \simeq \frac{2\pi}{\ln(8/KL)-2\gamma}. \tag{2.4.21}$$

With a considerable amount of extra work it would be possible to obtain the next term in the expansion but we do not consider this to be justified in terms of results or understanding of the problem. Finally, we note that with the initial approximation $k \sim (\pi f_D)^{1/2}$, (2.4.21) gives the same result as we obtained using the pseudo-effective medium approach.

2.5 Conclusion

We have shown ((2.2.13) and (2.2.47)), in the limit of small dislocation density and subject to the approximations described in section 2.2, that the overall sink strength of the array does not depend on the core boundary condition. We have also shown that, to lowest order, the pseudo-effective medium solution and the solution by matched asymptotic expansion are the same and that with a first approximation of $k = (\pi f_D)^{1/2}$ give the same result as the Heald-Speight model.

In the absence of an exact solution we believe that the method of matched expansions provides the best way of obtaining approximate solutions owing to its systematic nature and because it obviates the necessity of providing an artificial boundary.

3. The Effective Sink Strength of an Array of Dislocation Loops

3.1 Introduction

In this chapter we obtain estimates for the sink strength of arrays of dislocation loops. The core of the loops is assumed to be toroidal and this rather difficult geometry has limited past attempts to consider the problem analytically: Brailsford and Bullough (1972) and (1976) replaced the toroidal sink by a spherical sink of the same radius. Although they used a different boundary condition on the sink surface from the one we shall adopt, we shall show that in an appropriate limit, our analysis reproduces their result of 1976. More recently Bullough, Wells, Willis and Wood (1980) performed numerical calculations for the problem of a loop having a square cross section embedded in a sink free cylindrical cell, throughout which defects were introduced at a constant rate and with no flux of defects allowed across the outer boundary of the cell. They obtained results for a variety of loop and cell sizes and also allowed for interaction between the defects and the loop.

Our approach here is to try to get analytical estimates for the sink strength. We consider two different cell models and a self-consistent scheme. For each model we will treat the two cases of neutral loops, having no interaction energy, and loops having a short ranged interaction with the diffusing population. The first of our cell models consists of a loop embedded in a spherical sink free region. Defect production is simulated by a constant concentration condition on the cell boundary and the loop is assumed to be a perfect sink. This model is directly analogous to that of Heald and Speight (1975) for straight dislocations described in chapter 2. The second model is that of Bullough et al (1980), except that we assume a spherical rather than a cylindrical cell. The self-consistent scheme we adopt is the same as described in chapter 2.

Exact analytic solutions are unknown for any of the models we consider. Instead, we rely heavily on the method of matched asymptotic expansions. In consequence we are restricted to considering loops large enough for there to be no competition between opposite sides, and interaction fields which are short ranged in comparison to the loop radius. In addition, for the cell models, the cell radius must be large compared to the loop radius.

This latter restriction means we do not expect our results using the cell models to be valid except at low concentrations of loops. The self-consistent scheme for neutral loops is free of this constraint and we might expect it to have a greater range of validity. However when there is interaction between the loop and the defects the self-consistent calculation is subject to another restriction which we discuss later.

3.2 Cell Models without Drift

In this section we consider the two simplest cell models in which we assume that there is no interaction between the point defect and the dislocation loop. This is a reasonable approximation if the defect is a vacancy. The loop is assumed to be surrounded by a spherical sink free zone of radius R_c and for the first model the production of defects is simulated by a constant concentration boundary condition on the sphere surface while for the second defects are introduced at a constant rate in the sink free region.

The geometry of both models is a little complicated and is illustrated in figure 3.1. The loop is assumed to have radius a and its core to have radius of cross section ρ_0 . Three coordinate systems will be used : spherical polar coordinates having radial distance R, cylindrical polar coordinates (r, θ, z) relative to the axis perpendicular to the plane of the loop and coordinates (ρ, ϕ) centred on the core axis. Thus

$$r = a + \rho\cos\phi, \qquad (3.2.1)$$

$$z = \rho\sin\phi \qquad (3.2.2)$$

For the first model the concentration of defects c, normalized to the defect diffusivity D satisfies the differential equation

$$\nabla^2 c = 0, \quad x \in \Omega, \qquad (3.2.3)$$

Ω being the sink free region, together with the boundary conditions

$$c = 0, \quad \rho = \rho_0, \qquad (3.2.4)$$

and

$$C=1 \quad , \quad R=R_c . \tag{3.2.5}$$

We will look for solutions of (3.2.3) to (3.2.5) when both δ_0/a, $a/R_c \ll 1$, so we now write

$$c(r,z) = A + B\frac{R^2}{a^2} P_2(\cos\theta) + C\,\phi_1(r,z), \tag{3.2.6}$$

where P_2 is the Legendre polynomial of degree 2 and ϕ_1 gives the field due to a ring sink at the loop core, so

$$\phi_1(r,z) = a\int_0^{2\pi} \frac{d\theta}{[r^2+z^2+a^2+2ar\cos\theta]^{1/2}} . \tag{3.2.7}$$

The approximation (3.2.6) could be improved by adding a term involving the field due to a ring dipole; however such a term would be of order $(\delta_0/a)^2$ and so will not be considered here.

To apply the boundary conditions, the asymptotic behaviour of ϕ_1, is needed when $R/a \gg 1$ and when $\delta/a \ll 1$. The first of these is easy for, putting $r = R\sin\theta$, $z = R\cos\theta$

$$\phi_1(R,\theta) = a\int_0^{2\pi} \frac{d\theta'}{(R^2+a^2-2aR\sin\theta\cos\theta')^{1/2}} , \tag{3.2.8}$$

and expanding the integrand shows that for $R/a \gg 1$

$$\phi_1 \sim 2\pi\left\{\frac{a}{R} - \frac{1}{2}\frac{a^3}{R^3} P_2(\cos\theta)\right\}. \tag{3.2.9}$$

For the other limit ϕ_1 can be written in terms of the complete elliptic integral of the first kind K(k) (see for example Dwight (1964)) as

$$\phi_1(\rho,\phi) = \frac{4a}{(4a^2+\rho^2+4a\rho\cos\phi)^{1/2}} K(\kappa), \tag{3.2.10}$$

where

$$\kappa^2 = 1-\kappa'^2 , \tag{3.2.11}$$

and

$$\kappa'^2 = \frac{\rho^2}{4a^2 + \rho^2 + 4a\rho\cos\phi} \quad . \tag{3.2.12}$$

Now when $\kappa' << 1$

$$K(\kappa) \sim \ln\left(\frac{4}{\kappa'}\right) , \tag{3.2.13}$$

so that for $\rho/a << 1$

$$\phi_1 \sim 2\ln\left(\frac{8a}{\rho}\right) + \frac{\rho\cos\phi}{a}\left[2 - \ln\left(\frac{8a}{\rho}\right)\right]. \tag{3.2.14}$$

We can now apply the boundary conditions (3.2.4), (3.2.5) to the representation (3.2.6). Hence on $R = R_c >> a$

$$1 = A + 2\pi C\left(\frac{a}{R_c}\right) + \left(\beta\frac{R_c^2}{a^2} - \pi C\frac{a^3}{R_c^3}\right) P_2(\cos\theta), \tag{3.2.15}$$

which implies the relations

$$A = 1 - 2\pi C\frac{a}{R_c} , \tag{3.2.16}$$

and

$$\beta = \pi C\left(\frac{a}{R_c}\right)^5 . \tag{3.2.17}$$

Next, on $\rho = \rho_0 << a$

$$\frac{R^2}{a^2} P_2(\cos\theta) = \frac{z^2}{a^2} - \frac{1}{2}\frac{r^2}{a^2}$$

$$\sim -\frac{1}{2} - \frac{\rho_0}{a}\cos\phi , \tag{3.2.18}$$

so

$$A - \frac{B}{2}\left(1 + 2\frac{\delta_0}{a}\cos\phi\right) + C\left\{2\ln\left(\frac{\beta a}{\delta_0}\right) + \frac{\delta_0}{a}\cos\phi\left[2 - \ln\left(\frac{\beta a}{\delta_0}\right)\right]\right\}$$

$$= 0, \tag{3.2.19}$$

which in turn implies, to lowest order in δ_0/a,

$$A - \frac{B}{2} + 2C\ln\left(\frac{\beta a}{\delta_0}\right) = 0. \tag{3.2.20}$$

The solution of (3.2.16), (3.2.17) and (3.2.20) is now given by

$$C = -\left\{2\ln\left(\frac{\beta a}{\delta_0}\right) - 2\pi\left(\frac{a}{R_c}\right) - \frac{\pi}{2}\left(\frac{a}{R_c}\right)^5\right\}^{-1}, \tag{3.2.21}$$

$$B = -\pi\left(\frac{a}{R_c}\right)^5\left\{2\ln\left(\frac{\beta a}{\delta_0}\right) - 2\pi\left(\frac{a}{R_c}\right) - \frac{\pi}{2}\left(\frac{a}{R_c}\right)^5\right\}^{-1}, \tag{3.2.22}$$

and

$$A = 1 + \frac{2\pi\left(\frac{a}{R_c}\right)}{2\ln\left(\frac{\beta a}{\delta_0}\right) - 2\pi\left(\frac{a}{R_c}\right) - \frac{\pi}{2}\left(\frac{a}{R_c}\right)^5}. \tag{3.2.23}$$

The flux of defects into the dislocation is most easily determined by calculating the flux across $R=R_c$. On $R=R_c$ we find

$$\frac{\partial C}{\partial R} \sim -2\pi\frac{a}{R_c^2}C + P_2(\cos\theta)\left\{2B\frac{R_c}{a^2} + \pi C\frac{a^3}{R_c^4}\right\}. \tag{3.2.24}$$

Thus the total flux into the dislocation is given by

$$\int_{R=R_c} \frac{\partial c}{\partial R}\, ds = -8\pi a^2 C$$

$$= \frac{8\pi^2 a}{2\ln\left(\frac{8a}{\rho_0}\right) - 2\pi\left(\frac{a}{R_c}\right) - \frac{\pi}{2}\left(\frac{a}{R_c}\right)^5}, \qquad (3.2.25)$$

and so the flux per unit length of line F into the dislocation is

$$F = \frac{4\pi}{2\ln\left(\frac{8a}{\rho_0}\right) - 2\pi\left(\frac{a}{R_c}\right) - \frac{\pi}{2}\left(\frac{a}{R_c}\right)^5}. \qquad (3.2.26)$$

In order to evaluate the sink strength per unit length of line we first need the mean value of c over Ω. The first two terms in (3.2.6) are easily dealt with. As it is harmonic, the mean value of ϕ_1 can be found by expanding it in terms of spherical harmonics for $a<|x|<R_c$ and for $|x|<a$. In each case the only term that contributes is the first. We find

$$\int_{|x|<a} \phi_1\, dx = 2\pi \cdot \frac{4}{3}\pi a^3, \qquad (3.2.27)$$

and

$$\int_{a<|x|<R_c} \phi_1\, dx = 2\pi a \cdot 2\pi\left(R_c^2 - a^2\right). \qquad (3.2.28)$$

The integral of ϕ_1 over the torus $\rho<\rho_0$ can be found approximately using (3.2.14) so that we find

$$\overline{\phi_1} \sim \frac{1}{\frac{4}{3}\pi R_c^3 - 2\pi a^2 \rho_0^2}\left\{ 4\pi^2 R_c^2 a - \frac{4}{3}\pi^2 a^3 \right.$$

$$\left. - 4\pi^2 a \rho_0^2 \left(\ln\left(\frac{8a}{\rho_0}\right) + \frac{1}{2}\right)\right\}, \qquad (3.2.29)$$

which to lowest order in δ_0/a gives

$$\bar{\phi}_1 \sim \pi \left\{ 3\left(\frac{a}{R_c}\right) - \left(\frac{a}{R_c}\right)^3 \right\}. \qquad (3.2.30)$$

Finally, then, use of (3.2.30), (3.2.16) in (3.2.6) implies that

$$\bar{c} \sim 1 + \pi C \left\{ \left(\frac{a}{R_c}\right) - \left(\frac{a}{R_c}\right)^3 \right\}, \qquad (3.2.31)$$

so that the sink strength per unit length of line Z is given by

$$Z = F / \bar{c}$$

$$= \frac{2\pi}{\ln\left(\frac{8a}{\delta_0}\right) - \frac{3\pi}{2}\left(\frac{a}{R_c}\right) + \frac{\pi}{2}\left(\frac{a}{R_c}\right)^3 - \frac{\pi}{4}\left(\frac{a}{R_c}\right)^5}. \qquad (3.2.32)$$

For the second model considered in this section, defects are introduced at a constant rate K throughout Ω so that the concentration c satisfies

$$\nabla^2 c + K = 0, \quad x \in \Omega, \qquad (3.2.33)$$

and

$$c = 0, \quad \delta = \delta_0. \qquad (3.2.34)$$

The appropriate condition on $R=R_c$ is now

$$\frac{\partial c}{\partial R} = 0, \quad R = R_c, \qquad (3.2.35)$$

so that the dislocation is the only sink for the defects.

Integrating (3.2.33) over Ω we see immediately that the total flux of defects into the dislocation per unit length of line is

$$F = \frac{K}{2\pi a}\left(\frac{4}{3}\pi R_c^3 - 2\pi^2 a f_0^2\right). \tag{3.2.36}$$

We now write

$$C(r,z) = -\frac{KR^2}{6} + A + B\frac{R^2}{a^2}P_2(\cos\theta) + C\phi_1(r,z), \tag{3.2.37}$$

so that use of (3.2.9) and the boundary condition (3.2.35) shows that

$$0 = -\frac{KR_c}{3} - 2\pi C\frac{a}{R_c^2} + \left(2B\frac{R_c}{a^2} + 3\pi C\frac{a^3}{R_c^4}\right)P_2(\cos\theta), \tag{3.2.38}$$

for which B and C are obtained as

$$C = -\frac{KR_c^3}{6\pi a}, \tag{3.2.39}$$

and

$$B = \frac{KR_c^3}{4a}\left(\frac{a}{R_c}\right)^5. \tag{3.2.40}$$

Application of the core boundary condition and neglect of terms of order f_0/a implies

$$-\frac{Ka^2}{6} + A - \frac{B}{2} + 2C\ln\left(\frac{\gamma a}{f_0}\right) = 0, \tag{3.2.41}$$

so that A is given by

$$A = \frac{Ka^2}{6}\left\{1 + \frac{3}{4}\left(\frac{a}{R_c}\right)^2 + \frac{2}{\pi}\left(\frac{R_c}{a}\right)^3\ln\left(\frac{\gamma a}{f_0}\right)\right\}. \tag{3.2.42}$$

The mean value of c is now given approximately by

$$\bar{c} \sim -\frac{KR_c^2}{10} + A + C\bar{\phi}_1$$

$$\sim \frac{KR_c^3}{3\pi a}\left\{\ln\left(\frac{\gamma a}{f_0}\right) - \frac{9\pi}{5}\left(\frac{a}{R_c}\right) + \pi\left(\frac{a}{R_c}\right)^3 + \frac{3\pi}{8}\left(\frac{a}{R_c}\right)^5\right\}, \tag{3.2.43}$$

so that the sink strength per unit length of line is given by

$$Z = \frac{2\pi}{\left\{ \ln\left(\frac{8a}{f_0}\right) - \frac{9\pi}{5}\left(\frac{a}{R_c}\right) + \pi\left(\frac{a}{R_c}\right)^3 + \frac{3\pi}{8}\left(\frac{a}{R_c}\right)^5 \right\}} \qquad (3.2.44)$$

We can make contact with the work of Brailsford and Bullough (1976) at this point by noting that, in the limit $a/R_c \to 0$ both (3.2.32) and (3.2.44) reduce to

$$Z = 2\pi / \ln\left(\frac{8a}{f_0}\right). \qquad (3.2.45)$$

Brailsford and Bullough replaced the toroidal sink by an equivalent sphere and imposed a rate control condition like (2.1.5) on its surface. They scaled the result obtained for the sphere using the capacitance of a charged torus given by Siedman and Balluffi (1966). In the limit $\alpha \to \infty$ the rate control condition becomes c=0 and their estimate for Z reduces to (3.2.45). Thus at low concentrations of sinks we have some evidence to suggest that their approximation is a reasonable one.

3.3 Cell Models with Drift

We now turn to the more difficult problem of diffusion of interstitial atoms to a loop sink. There is now an interaction between the dislocation loop and the interstitial. In the absence of externally applied stress, the energy of interaction E_1 was given by Bastecka and Kroupa (1964) and can be written in the form

$$\frac{E_1}{E'} = \frac{-L}{\left((r+a)^2+z^2\right)^{1/2}} \left[\frac{a^2-r^2-z^2}{(a-r)^2+z^2} E(k) + K(k) \right], \qquad (3.3.1)$$

where $E'=\kappa T$, k Boltzman's constant, T temperature, is the thermal energy, L is given by (2.2.10)

$$\kappa = \left\{ \frac{4ar}{((r+a)^2+z^2)} \right\}^{1/2}, \tag{3.3.2}$$

amd K(k), E(k) are complete elliptic integrals of the first and second kinds. As in § 3.2, in the first model we consider, the defects are introduced through the outer boundary and requiring that the flux of defects be zero in Ω implies that

$$\nabla\left(\nabla c + \frac{c}{E'}\nabla E_1\right) = 0 \quad , \quad x \in \Omega, \tag{3.3.3}$$

which, because E_1/E' is harmonic, can be written

$$\nabla^2 c + \nabla c . \nabla\left(\frac{E_1}{E'}\right) = 0. \tag{3.3.4}$$

The boundary conditions on the core and cell boundary are again given by (3.2.4) and (3.2.5). Equation (3.3.4) is now transformed using the change of variables of Margvelashvili and Saralidze (1974)

$$c = \psi e^{-E_1/2E'} \quad , \tag{3.3.5}$$

to get

$$\nabla^2\psi - \frac{1}{4}\psi\left(\nabla\left(\frac{E_1}{E'}\right)\right)^2 = 0 \quad , \tag{3.3.6}$$

where ψ now satisfies

$$\psi = e^{E_1/2E'}, \quad R = R_c . \tag{3.3.7}$$

Next, when $\delta/2a \ll 1$ use of the small argument expressions for E(k) and K(k) given by Dwight shows that

$$E_1/E' \sim V = \frac{L\cos\phi}{\delta} \tag{3.3.8}$$

the terms neglected being O(1).

When $R/2a \gtrsim 1$ Bullough and Newman (1970) give the result

$$\frac{E_1}{E'} \sim \frac{La^2}{R^3} P_2(\cos\theta). \tag{3.3.9}$$

We thus see that the interaction is short ranged and decays rapidly at large distances from the loop. In consequence we now set

$$\varepsilon = L/a, \tag{3.3.10}$$

$$E_1/E' = \varepsilon U, \tag{3.3.11}$$

where

$$U \sim \frac{a\cos\phi}{\rho} \tag{3.3.12}$$

when $\rho/a \ll 1$ and try to solve (3.3.6) in the limit $\varepsilon \to 0$ using the method of matched asymptotic expansions.

First we note that when ρ/a is O(1), U=O(1) so that the second term in (3.3.6) is $O(\varepsilon^2)$ and can be neglected. This gives for the outer problem

$$\nabla^2\psi_0 = 0. \tag{3.3.13}$$

Also the exponent in (3.3.7) is $O(\varepsilon)$ so that this boundary condition is replaced by

$$\psi_0 = 1, \quad R = R_c. \tag{3.3.14}$$

Then if we try a solution of the form

$$\psi_0 = A + B\frac{R^2}{a^2} P_2(\cos\theta) + C\phi_1(r,z), \tag{3.3.15}$$

use of (3.3.14) leads to the relations

$$A = 1 - 2\pi C\left(\frac{a}{R_c}\right), \tag{3.3.16}$$

and

$$B = \pi C\left(\frac{a}{R_c}\right)^5. \tag{3.3.17}$$

Next, when ρ/a is $O(\varepsilon)$ we write

$$\rho = \varepsilon \rho' \tag{3.3.18}$$

and in terms of ρ and ϕ

$$\nabla^2\psi - \frac{1}{4}\psi(\nabla V)^2 = \nabla_2^2\psi - \frac{1}{4}\psi(\nabla_2\psi)^2 + \frac{1}{a+\rho\cos\phi}\left\{\cos\phi\,\frac{\partial\psi}{\partial\rho} - \frac{\sin\phi}{\rho}\,\frac{\partial\psi}{\partial\phi}\right\}, \tag{3.3.19}$$

where ∇_2^2, ∇_2 are two dimensional operators. Hence in terms of ρ', the first two terms in (3.3.19) are $O(1/\varepsilon^2)$ and the third is $O(1/\varepsilon)$ and so to lowest order the inner problem is

$$\nabla_2^2\psi_i - \frac{1}{4}\psi_i(\nabla_2 V)^2 = 0\,, \tag{3.3.20}$$

$$\psi_i = 0\,, \quad \rho = \rho_0\,, \tag{3.3.21}$$

from which we see that close to the loop it behaves as a straight dislocation. A solution of (3.3.20) and (3.3.21) dependent on ρ only is

$$\psi_i(\rho,\phi) = D\left\{K_0\left(\frac{L}{2\rho}\right)I_0\left(\frac{L}{2\rho_0}\right) - I_0\left(\frac{L}{2\rho}\right)K_0\left(\frac{L}{2\rho_0}\right)\right\}. \tag{3.3.22}$$

To invoke the matching principle of Van Dyke (1964) we expand (3.3.22) to lowest order when $\rho \gg 1$ to get for the outer expansion of the inner solution ψ_i^o, with γ Euler's constant,

$$\psi_i^o \sim D\left[\left[-\ln\left(\frac{L}{4\rho}\right) - \gamma\right]I_0\left(\frac{L}{2\rho_0}\right) - K_0\left(\frac{L}{2\rho_0}\right)\right], \tag{3.2.23}$$

and to get the inner expansion of the outer solution we write (3.3.15) in terms of inner variables ρ', ϕ and expand to lowest order in ε. The result expressed in outer variables ρ, ϕ is

$$\psi_0^i \sim A - \frac{B}{2} + 2C\ln\left(\frac{\gamma a}{\rho}\right). \tag{3.3.24}$$

The right sides of (3.3.23), (3.3.24) should agree, so that equating constants and coefficients of $\ln(\rho)$ we find

$$A - \frac{B}{2} + 2C\ln(\beta a) = -D\left\{\left(\ln\left(\frac{L}{4}\right)+\gamma\right)I_0\left(\frac{L}{2\rho_0}\right) + K_0\left(\frac{L}{2\rho_0}\right)\right\}, \tag{3.3.25}$$

and

$$2C = -D\, I_0\left(\frac{L}{2\rho_0}\right). \tag{3.3.26}$$

The solutions to (3.3.16), (3.3.17), (3.3.25) and (3.3.26) for A, B, D can all be expressed in terms of C which is easily found to be given by

$$2C\left\{\ln\left(\frac{L}{32a}\right) + \gamma + \left(K_0(\tfrac{1}{2}\rho_0)\big/ I_0(\tfrac{1}{2}\rho_0)\right)\right.$$

$$\left. + \pi\left(\frac{a}{R_c}\right) + \frac{\pi}{4}\left(\frac{a}{R_c}\right)^5\right\} = 1. \tag{3.3.27}$$

The flux per unit length of line into the dislocation is calculated in the same way as in the last section and is again given by

$$F = -4\pi C \tag{3.3.28}$$

To evaluate $\bar{c}$ we express c as the composite series

$$c \sim e^{-E_1/2\varepsilon'}\left\{\psi_1 + \psi_0 - \psi_1^0\right\}. \tag{3.3.29}$$

Then, noting that when $\rho > a\varepsilon^{1/2}$ $\psi_i - \psi_i^0$ is $O(\varepsilon)$, the mean value of $e^{-E_1/2\varepsilon'}(\psi_i - \psi_i^0)$ is given approximately by

$$\frac{3a}{2R_c^3}\int_0^{2\pi} d\phi \int_{\rho_0}^{a\varepsilon^{1/2}} e^{-V/2}\left\{\psi_i - \psi_i^0\right\}\rho\, d\rho, \tag{3.3.30}$$

which is bounded by $\varepsilon\left(\frac{a}{R_c}\right)^3$ times a constant.

Thus the dominant contribution to c comes from the outer solution and we find, as in §3.2,

$$\bar{C} \sim 1 + \pi C \left\{ \left(\frac{a}{R_c}\right) - \left(\frac{a}{R_c}\right)^3 \right\}. \tag{3.3.31}$$

Finally, the sink strength per unit length of line is given by

$$Z = \frac{2\pi}{\ln\left(\frac{32a}{L}\right) - \gamma - \left(K_0(\tfrac{1}{2}\beta_0)/I_0(\tfrac{1}{2}\beta_0)\right) - \frac{3\pi}{2}\left(\frac{a}{R_c}\right) + \frac{\pi}{2}\left(\frac{a}{R_c}\right)^3 - \frac{\pi}{4}\left(\frac{a}{R_c}\right)^5} \tag{3.3.32}$$

For the second model where defects are introduced at a constant rate K throughout Ω the inner solution is still given by (3.3.22) while the outer solution is now

$$\psi_0 = -\frac{KR^2}{6} + A + B\frac{R^2}{a^2} P_2(\cos\theta) + C\,\phi_1(r,z), \tag{3.3.33}$$

for which the no flux condition across $R=R_c$ implies, as $L/R_c \ll 1$,

$$C = -\frac{KR_c^3}{6\pi a}, \tag{3.3.34}$$

and

$$B = \frac{KR_c^3}{4a}\left(\frac{a}{R_c}\right)^5. \tag{3.3.35}$$

The inner limit of the outer solution is now given by

$$\psi_0^{\,i} \sim -\frac{Ka^2}{6} + A - \frac{B}{2} + 2C\ln\left(\frac{8a}{\rho}\right), \tag{3.3.36}$$

so that, matching this to (3.3.23), we find

$$-\frac{Ka^2}{6} + A - \frac{B}{2} + 2C\ln 8a = -D\left\{\left[\ln\left(\frac{L}{4}\right) + \gamma\right] I_0\left(\frac{L}{2\beta_0}\right) + K_0\left(\frac{L}{2\beta_0}\right)\right\}, \tag{3.3.37}$$

and

$$2C = -D I_0\left(\tfrac{L}{2}\gamma_0\right). \tag{3.3.38}$$

The only constant still needed explicitly is A, which is easily found to be given by

$$A = \frac{Ka^2}{6} + \frac{Ka^2}{8}\left(\frac{a}{R_c}\right)^2 + \frac{KR_c^3}{3\pi a}\left\{\ln\left(\frac{32a}{L}\right) - \gamma - \frac{K_0(\tfrac{1}{2}\gamma_0)}{I_0(\tfrac{1}{2}\gamma_0)}\right\}. \tag{3.3.39}$$

The flux into the dislocation is given approximately by

$$F = \frac{4}{3}\pi R_c^3 K, \tag{3.3.40}$$

and the average concentration by

$$\bar{C} \sim -\frac{KR_c^2}{10} + A + \pi C\left\{3\left(\frac{a}{R_c}\right) - \left(\frac{a}{R_c}\right)^3\right\}; \tag{3.3.41}$$

substituting for A and C in (3.3.41) we find

$$\bar{C} = \frac{KR_c^3}{3\pi a}\left\{\ln\left(\frac{32a}{L}\right) - \gamma - \frac{K_0(\tfrac{1}{2}\gamma_0)}{I_0(\tfrac{1}{2}\gamma_0)} - \frac{9\pi}{5}\left(\frac{a}{R_c}\right) + \pi\left(\frac{a}{R_c}\right)^3 + \frac{3\pi}{8}\left(\frac{a}{R_c}\right)^5\right\}, \tag{3.3.42}$$

and hence the sink strength per unit length of line is

$$Z = \frac{2\pi}{\ln\left(\frac{32a}{L}\right) - \gamma - \frac{K_0(\tfrac{1}{2}\gamma_0)}{I_0(\tfrac{1}{2}\gamma_0)} - \frac{9\pi}{5}\left(\frac{a}{R_c}\right) + \pi\left(\frac{a}{R_c}\right)^3 + \frac{3\pi}{8}\left(\frac{a}{R_c}\right)^5}. \tag{3.3.43}$$

3.4 Self-Consistent Calculations

As in chapter 2 we now assume that a random distribution of sinks can be replaced by a continuous distribution of point sinks of strength k^2. We embed one dislocation loop into this continuous distribution and estimate k^2 self-consistently by equating the flux of defects into the dislocation to $\kappa^2\bar{c}/n_D$ where n_D is the dislocation density. The equation governing the concentration c is

$$\nabla^2 c + \frac{1}{f}\nabla c.\nabla E_1 - \kappa^2 c + \kappa^2 = 0, \qquad (3.4.1)$$

with boundary conditions

$$c = 0, \quad \rho = \rho_0, \qquad (3.4.2)$$

and

$$c \to \bar{c} = 1, \quad R \to \infty, \qquad (3.4.3)$$

the generation rate of defects having been normalized so that $\bar{c} = 1$. E_1 has been assumed to be harmonic.

Once again we will consider two problems: the first when the interaction term is zero, the second when it is present but short ranged and has the form (3.3.11). When there is no interaction the second term in (3.4.1) is zero and, as in §2, we assume that the loop can be treated approximately as a ring sink centred at the origin lying in the x, y plane. We thus try as a solution,

$$c = 1 + A\int_{\rho=a} \frac{e^{-\kappa|x-x'|}}{|x-x'|}\,dx', \qquad (3.4.4)$$

where A is to be determined from (3.4.2). It will be convenient to call the integral in (3.4.4) c_1; then writing it in terms of cylindrical polar coordinates (r,θ,z) and making the change of variables $y = \cos\theta/2$ it can be written in terms of normalized variables $\rho' = \rho/a$, $r' = r/a$ as

$$c_1 = 4\int_0^1 \frac{e^{-\kappa a t}}{(1-y^2)^{1/2} t}\,dy, \qquad (3.4.5)$$

where

$$t = (\rho'^2 + 4r'y^2)^{1/2}. \qquad (3.4.6)$$

The boundary condition (3.4.2) now implies

$$A = -1/c_1(f_0') \quad , \quad f_0' = f_0/a \quad , \tag{3.4.7}$$

so that for $f_0/a \ll 1$ the difficulty is to evaluate (3.4.5.) in the limit $f' \to 0$, $r \to a$. As a first step we approximate the integral using the method of Fraenkel (1969): the integrand $f(y,f')$ is expanded in a composite series so that if f^o is a one term outer series valid when $y \gg f'$, f^i is a one term inner series valid when $y = O(f')$ and f_o^i denotes the one term inner expansion of the outer series

$$f \sim f^o + f^i - f_o^i \quad , \tag{3.4.8}$$

provided that $f_o^i = f_i^o$. The integral is then estimated as the integral of the right side of (3.4.8).

When $y \gg f$ the expansion is easy and we get

$$f^o(y,f') = \frac{e^{-\kappa a r'^{1/2} y}}{(1-y^2)^{1/2}\, 2 r'^{1/2} y} \quad . \tag{3.4.9}$$

When $y = O(f')$ we introduce the variable transformation

$$y = f'x \quad , \tag{3.4.10}$$

and expand f to lowest order in f' to get

$$f^i(x,f') = \frac{1}{f'[1+4r'x^2]^{1/2}} \quad . \tag{3.4.11}$$

The inner expansion of the outer series is found by writing (3.4.9) in term of the inner variable x and expanding in powers of f' so that

$$f_o^i = 1/(2r'^{1/2} f'x) \quad , \tag{3.4.12}$$

and similarly the outer expansion of the inner series is found by writing (3.4.11) in terms of the outer variable y and expanding to get

$$f_i^o = 1/(2r'^{1/2} y) \quad . \tag{3.4.13}$$

Thus we see that $f_o^i = f_i^o$ and so (3.4.8) obtains. Forming the composite series and integrating we find for c_1

$$c_1 \sim c_2 + c_3 \,, \tag{3.4.14}$$

where

$$c_2 = \frac{2}{r'^{1/2}} \int_0^1 \left\{ \frac{e^{-2\kappa a r'^{1/2} y}}{(1-y^2)^{1/2}} - 1 \right\} \frac{dy}{y} \,, \tag{3.4.15}$$

and

$$c_3 = 4 \int_0^1 \frac{dy}{t} \,. \tag{3.4.16}$$

The integral in (3.4.16) is easy and to lowest order in ρ' is

$$c_3 \sim \frac{2}{r'^{1/2}} \log \frac{4 r'^{1/2}}{\rho'} \,. \tag{3.4.17}$$

Also as we are interested in c_1 when $\rho' = \rho_0/a \ll 1$ and $r' = 1 + \frac{\rho_0}{a} \cos\phi$ we can put $r' = 1$ in (3.4.17) (and (3.4.15)) to get

$$c_3 \sim 2 \log(4/\rho') \,, \tag{3.4.18}$$

and

$$c_2 \sim 2 \int_0^1 \left\{ \frac{e^{-2\kappa a y}}{(1-y^2)^{1/2}} - 1 \right\} \frac{dy}{y} \,. \tag{3.4.19}$$

For arbitrary ka this integral would have to be evaluated numerically. However, in the two limits $\kappa a \ll 1$ and $\kappa a \gg 1$ further analytic progress is possible.

First if $\kappa a \ll 1$, the exponential can be expanded to first order in ka and the result integrates to get

$$c_2 \sim 2 \log 2 - 4 \pi \kappa a \,. \tag{3.4.20}$$

second when $\kappa a \gg 1$ we split the range of integration into two parts: from 0 to $(\kappa a)^{-1/2}$ and from $(\kappa a)^{-1/2}$ to 1. Then, writing $\lambda = (\kappa a)^{-1/2}$, we get

$$c_2 \sim 2\int_0^{\lambda}\left(\frac{e^{-2\kappa a y}-1}{y}\right)dy - 2\int_{\lambda}^{1}\frac{dy}{y}$$

$$+\int_0^{\lambda} y\, e^{-2\kappa a y}\,dy + 2\int_{\lambda}^{1}\left(\frac{e^{-2\kappa a y}}{(1-y^2)^{1/2}}-1\right)\frac{dy}{y}. \qquad (3.4.21)$$

The fourth integral in (3.4.21) tends to zero as $\kappa a \to \infty$ like $(\kappa a)^{1/2} e^{-2(\kappa a)^{1/2}}$ while the third is $O((\kappa a)^{-2})$ so both are neglected. The second integral is trivial so we are left with the first. We make the change of variables $x = 2\kappa a y$ and integrate by parts to get first

$$-2\log\frac{2}{\lambda} + 2\int_0^{\infty} e^{-x}\log x\,dx - 2\int_{2/\lambda}^{\infty} e^{-x}\log x\,dx, \qquad (3.4.22)$$

and a further integration by parts shows that the second integral in (3.4.22) is negligible as $\lambda \to 0$. The other integral gives $-\gamma$, γ Euler's constant, so that finally

$$c_2 \sim -2\log(2\kappa a) - 2\gamma \qquad (3.4.23)$$

Summarizing, we have the two estimates for c_1 as $f' \to 0$:

$$c_1 \sim 2\log\frac{8}{f'} - 4\pi\kappa a \quad , \quad \kappa a \ll 1, \qquad (3.4.24)$$

and

$$c_1 \sim 2\log\frac{4}{f'} - 2\gamma - 2\log(2\kappa a), \quad \kappa a \gg 1. \qquad (3.4.25)$$

The boundary condition on $f' = f_0/a$ can now be applied and we get for the constant A:

$$A \sim -1\Big/\left\{2\log\left(\frac{8a}{f_0}\right)\right\} \quad , \quad \kappa a \ll 1, \qquad (3.4.26)$$

and

$$A \sim -1\Big/\left\{2\log\left(\frac{2}{\kappa f_0}\right) - 2\gamma\right\}, \quad \kappa a \gg 1, \qquad (3.4.27)$$

where the term $4\pi\kappa a$ has been neglected in (3.4.26).

For general ka

$$A \sim -1 \Big/ \left\{ 2 \log\left(\frac{4a}{\gamma_0}\right) + c_2 \right\}, \tag{3.4.28}$$

where c_2 is given by (3.4.19). The flux into the dislocation is given by

$$J = -\nabla c_1 , \tag{3.4.29}$$

which is approximately

$$J = -2\pi A / \gamma , \tag{3.4.30}$$

so that the sink strength per unit length of line is given by

$$Z = -4\pi A . \tag{3.4.31}$$

We now obtain the overall sink strength self-consistently from the relation

$$K^2 = n_D Z , \tag{3.4.32}$$

with Z given by (3.4.31).

If we use (3.4.26) and (3.4.27) we get, when $ka \ll 1$,

$$Z \sim 2\pi / \log\left(\frac{\gamma a}{\gamma_0}\right), \tag{3.4.33}$$

and when $ka \gg 1$,

$$Z \sim 2\pi \Big/ \left\{ \log\left(\frac{2}{K\gamma_0}\right) - \gamma \right\}. \tag{3.4.34}$$

We note that (3.4.33) can be obtained from (3.2.32) in the limit of the cell size becoming infinite. This is not too surprising as in the limit $(ka)^2 \to 0$ equation (3.4.1) without the drift term becomes Laplace's equation. The other result, (3.4.34), bears some similarity to the solution for a straight edge dislocation embedded in a lossy medium. In this case, with K_0 the modified Bessel function,

$$Z = 2\pi / K_0(\kappa \rho_0), \tag{3.4.35}$$

and using the small argument expansion of K_0 reproduces (3.4.30) exactly. However in the present case it is not clear that $\kappa \rho_0$ is small enough to justify this process.

We now return to the full equation (3.4.1) and attempt to find an approximate solution using matched expansions. First it will be convenient to write

$$\frac{E_1}{E'} = \frac{L}{a} W\left(\frac{\rho}{a}\right), \tag{3.4.36}$$

so that if we make the change of variables

$$\rho = a x, \tag{3.4.37}$$

W is a function of x only and (3.4.1) becomes

$$\nabla^2 c + \nabla c \cdot \nabla\left(\frac{LW}{a}\right) - (\kappa a)^2 c + (\kappa a)^2 = 0, \tag{3.4.38}$$

and the core boundary condition is now

$$c = 0 \quad , \quad x = \rho_0/a . \tag{3.4.39}$$

When $L/a \ll 1$ and x = O(1), W = O(1) and the second term in (3.4.38) can be neglected. Thus in the outer region we solve

$$\nabla^2 c - (\kappa a)^2 c + (\kappa a)^2 = 0. \tag{3.4.40}$$

In the inner region, when $x = O(L/a)$,

$$W \sim \frac{\cos\phi}{x}, \tag{3.4.41}$$

so that the approximation (3.4.40) is no longer valid. In this region we set

$$x = \frac{L}{a} y, \tag{3.4.42}$$

so that a formal expansion of (3.4.38) and use of (3.4.41) implies

$$\nabla_y^2 c + \nabla_y c . \nabla\left(\frac{\cos\phi}{y}\right) - (kL)^2 (c-1) = 0. \qquad (3.4.43)$$

Hence, for $kL \ll 1$, in the inner region we study

$$\nabla_y^2 c + \nabla_y c . \nabla\left(\frac{\cos\phi}{y}\right) = 0. \qquad (3.4.44)$$

We now make the transformation of Margvelashvili and Saralidze in (3.4.44). Then, writing

$$c = \psi\, e^{-\frac{\cos\phi}{2y}}, \qquad (3.4.45)$$

and neglecting the contribution from the three dimensional geometry as in section 3, to lowest order the inner problem is

$$\nabla_2^2 \psi_1 - \frac{1}{4y^2}\psi_1 = 0. \qquad (3.4.46)$$

The solution to this inner problem was given in the last section; the outer limit is given in terms of the outer variable x by

$$\psi_1^0 = B\left[\left(-\ln\left(\frac{L}{4ax}\right) - \gamma\right) I_0\left(\frac{L}{2f_0}\right) - K_0\left(\frac{L}{2f_0}\right)\right]. \qquad (3.4.47)$$

This equation also gives the outer limit of c in the inner region, as the outer limit of $e^{-\cos\phi/2y} \sim 1$. The solution to the outer problem is given by (3.4.4) and the inner limit is, from (3.4.4), (3.4.5), (3.4.14) and (3.4.18)

$$c_0^1 = 1 + A\left[2\ln\left(\frac{4}{x}\right) + c_2(ka)\right], \qquad (3.4.48)$$

where we have noted the dependence of c_2 on ka.

Now c_2 is independent of x so matching coefficients of $\ln x$ we get

$$2A = -B I_0\left(\frac{L}{2f_0}\right), \tag{3.4.49}$$

and matching constants

$$B\left[\left(-\ln\left(\frac{L}{4a}\right)-\gamma\right) I_0\left(\frac{L}{2f_0}\right) - K_0\left(\frac{L}{2f_0}\right)\right] = 1 + A\left[2\ln 4 + c_2(ka)\right]. \tag{3.4.50}$$

Thus we find for A

$$A\left\{2\left[\ln\left(\frac{L}{16a}\right) + \gamma\right] + 2\,\frac{K_0(L/2f_0)}{I_0(L/2f_0)} - c_2(ka)\right\} = 1. \tag{3.4.51}$$

We only know how to estimate c_2 analytically when $ka \ll 1$ or $ka \gg 1$ and for these two cases we get

$$2A\left\{\left[\ln\left(\frac{L}{32a}\right) + \gamma\right] + \frac{K_0(L/2f_0)}{I_0(L/2f_0)}\right\} = 1, \quad ka \ll 1, \tag{3.4.52}$$

and

$$2A\left\{\left[\ln\left(\frac{kL}{8}\right) + 2\gamma\right] + \frac{K_0(L/2f_0)}{I_0(L/2f_0)}\right\} = 1, \quad ka \gg 1. \tag{3.4.53}$$

Finally, the flux into the dislocation is given by

$$J = -\left(\nabla c + c\,\nabla \frac{E_1}{E'}\right), \tag{3.4.54}$$

and using the inner limit of the outer solution this is approximately

$$J = -2A/f. \tag{3.4.55}$$

Thus the sink strength per unit length of line is

$$Z = -4\pi A, \tag{3.4.56}$$

where, in general, A is given by (3.4.51) .

The overall sink strength k^2 is obtained self-consistently from the relation

$$\kappa^2 = n_D Z, \tag{3.4.57}$$

and if we use (3.4.52) and (3.4.53) we get for $ka \ll 1$,

$$\kappa^2 = \frac{2\pi n_D}{\ln\left(\frac{32a}{L}\right) - \gamma - \left(K_0(1/2f_0)/I_0(1/2f_0)\right)}, \tag{3.4.58}$$

and for $\kappa a \gg 1$

$$\kappa^2 = \frac{2\pi n_D}{\ln\left(\frac{8}{\kappa L}\right) - 2\gamma - \left(K_0(1/2f_0)/I_0\left(\frac{L}{2f_0}\right)\right)}. \tag{3.4.59}$$

We see that (3.4.58) is the estimate obtained using the cell model with constant concentration boundary condition as $a/R_c \to 0$. Also (3.4.59) is exactly the estimate obtained in chapter 2, § 4, using matched expansions for the overall sink strength of an array of straight dislocations. Restrictions on the use of (3.4.58) and (3.4.59) will be discussed in the next section.

The condition $\kappa L \ll 1$ warrants some discussion. At low concentrations we expect that

$$\kappa^2 \sim n_D . \tag{3.4.60}$$

Then

$$\kappa L \sim (n_D f_0^2)^{1/2} \frac{L}{f_0}, \tag{3.4.61}$$

and taking $f_0 = 3 \times 10^{-8}$ cm and $n_D = 10^{11}$ cm/cm^3 , we get

$$\kappa L \sim .01 \left(\frac{L}{f_0}\right). \tag{3.4.62}$$

Thus to keep $\kappa L \ll 1$ we need $L/\ell_0 \lesssim 10$ and we are led to expect that our approximations are only valid when there is a weak interaction between the defect and the loop.

3.5 Results and Discussion

In this section we compare the results obtained using the various models considered so far. For the model where defects are introduced throughout the sink free region, Bullough et al (1980) have performed exact numerical calculations using the full form of the interaction energy (3.3.1). However, the majority of their results are for parameter values outside the range of validity of our approximations. Specifically, they allow long range interaction energies which affect the whole cell. Another drawback to any comparison is their use of a cylindrical cell.

Despite these objections, in figures 3.2 and 3.3 we have plotted the sink strength per unit length of line against a/ℓ_0 for the two models of defect production. Figure 3.2 was produced using (3.2.32) to get Z_1 and (3.3.32) with $L/\ell_0 = 20$ to get Z_2. Figure 3.3 was obtained using (3.2.44) and (3.3.43). For both figures a cell size $R_c/\ell_0 = 60$ was assumed. Also shown is the bias, $Z_2 - Z_1$. Our approximate scheme is not really valid for these parameters as it is only in the range $20 < a/\ell_0 < 30$ that $L/a < 1$ and $R_c/a > 2$. Nevertheless comparison of figure 3.3with the results of Bullough et al shows that in this range Z_1 is in approximate agreement with, while Z_2 (and hence the bias) is approximately three times greater than their results. We do not attach any great significance to this discrepancy as in this range we would expect interactions between opposite sides of the loop and between the loop and the boundary still to be significant. A further source of error could be the difference in cell and core geometries. Comparison of figures 3.2 and 3.3 shows that both models of defect production produce similar results.

In figures 3.4 and 3.5 results are shown for a cell size $R_c/\ell_0 = 100$. Figure 3.4 was produced using (3.2.32) to get Z_1 and (3.3.32) with $L/\ell_0 = 10$ to get Z_2. Figure 3.5 was obtained using (3.2.44) and (3.3.43). The bias is also shown. Again, we see that there is little difference between the results obtained using the two models of defect production. Referring to figure 3.5, we also see that, qualitatively, both Z_1 and Z_2 display the same characteristics as the results displayed by Bullough et al: the sink strengths both decrease before increasing with a/ℓ_0. The bias also has this property, although in all cases their results showed it to be

monotonic increasing. However in figure 3.5 it is increasing for $a/\rho_0 \gtrsim 20$: for smaller values of a/ρ_0 , $L/a > .5$ and we would not expect our results to be reliable. Finally we note that the dislocation density n_D is obtained from

$$n_D = 2\pi a \Big/ \left(\frac{4}{3}\pi R_c^3\right), \tag{3.5.1}$$

so that, assuming a core radius $\rho_0 = 3\times10^{-8}$ cm, the range $20 \lesssim a/\rho_0 \lesssim 50$ in figures 3.4 and 3.5 corresponds to

$$3.3\times10^{10} \lesssim n_D \lesssim 8.6\times10^{10} \text{ cm/cm}^3. \tag{3.5.2}$$

That is for each a/ρ_0 figures 3.4 and 3.5 provide estimates for the sink strength at a specific dislocation density in the range (3.5.2).

We now discuss the self-consistent estimates obtained in § 5. We first assess the validity of the approximations (3.4.20) and (3.4.23) to the integral c_2 given by (3.4.19). In figure 3.6 we have plotted the approximations (3.4.20) and (3.4.23) obtained when $\kappa a \ll 1$ and $\kappa a \gg 1$ respectively against ka, together with the result of a numerical evaluation of (3.4.19). We can see from this figure that (3.4.20) is only valid for $\kappa a \lesssim .02$ while (3.4.23) is a reasonable estimate for $\kappa a \gtrsim .5$. This will be borne out in the sequel.

For all the following results we took $\rho_0 = 3\times10^{-8}$ cm and in each case we express the outcome of the calculations in terms of the normalized sink strength per unit length of line Z, given by

$$Z = \kappa^2 / n_D \tag{3.5.3}$$

where k^2 is obtained as the result of a self-consistent calculation.

First when there is no drift field present the equation to solve for k is (3.4.32) with A given by (3.4.26) when $\kappa a \ll 1$, (3.4.27) when $\kappa a \gg 1$ and for arbitrary ka by (3.4.28). In figure 3.7 we have plotted Z against n_D for various values of a/ρ_0 and for the two estimates for A, (3.4.27) and (3.4.28). If the estimate (3.4.26) for A is used we get, when

$$\begin{aligned} Z = \quad & 1.7 \quad , \quad a/\ell_0 = 5 \quad , \\ & 1.24 \quad , \quad 20 \quad , \\ & 1.05 \quad , \quad 50 \quad , \\ & .94 \quad , \quad 100 \, . \end{aligned} \tag{3.5.4}$$

These results coincide with those obtained from the cell models in the limit $a/R_c \ll 1$.

We see from figure 3.7 that there is fair agreement between the estimates for the sink strengths when $a/\ell_0 \gtrsim 20$ and $n_D \gtrsim 5 \times 10^{10} \text{cm/cm}^3$, indicating that high concentrations of loops behave as straight dislocations. We also see that the approximation (3.4.27), obtained in the limit $\kappa a \gg 1$, is appropriate to large loops or high concentrations of loops, while comparison of (3.5.4) with figure 3.7 shows that the other limit, $\kappa a \ll 1$ is appropriate to small loops or low concentrations of loops. At $n_D = 5 \times 10^{10} \text{cm/cm}^3$ the values of κa are .2 and .7 for a/ℓ_0 = 20 or 100 and $\kappa a \sim .04$ for a/ℓ_0 = 5.

In figure 3.8 we have plotted the estimates for the sink strength given by the solution of (3.4.56) and (3.4.57) for various values of a/ℓ_0 and L/ℓ_0 = 10. using the estimate (3.4.51) for A. Also shown is the estimate appropriate to $\kappa a \gg 1$ obtained from (3.4.59). As a more extreme case we have also shown the results when a/ℓ_0 = 100 and L/ℓ_0 = 5. When $\kappa a \ll 1$ we get, from (3.4.58), for $L/\ell_0 = 10$

$$\begin{aligned} Z = \quad & 1.75 , \quad a/\ell_0 = 20 , \\ & 1.40 , \quad 50 , \\ & 1.21 \quad 100 , \end{aligned} \tag{3.5.5}$$

and when L/ℓ_0 = 5, a/ℓ_0 = 100

$$Z = 1.07 \tag{3.5.6}$$

As for the no-drift case there is fair agreement with (3.5.5) and (3.5.6) at low concentrations.

We see from figure 3.8 that, for large loops or high concentrations, the estimates obtained in the limit $\kappa a \gg 1$ agree reasonably well with those obtained using (3.4.51). However, the criterion $\kappa L \ll 1$ restricts the range of validity of our results.

For the parameters chosen, $\kappa L \sim .1$ when $n_D = 10^{11}$ cm/cm^3 which is consistent with (3.4.62). However the reliability of our estimates is in some doubt for higher concentrations. We are thus led to conclude that estimates obtained in the limit $\kappa a \gg 1$ are only appropriate to large loops. Also the other restriction that L/a be less than one indicates that the opposite limit, $\kappa a \ll 1$, is appropriate to low concentrations of loops.

In figures 3.9 and 3.10 we have compared the results obtained using cell models with self-consistent estimates using (3.4.51). Except at low concentrations, the agreement between the results is not good. In all cases shown on figures 3.9 and 3.10, $R_c/a \gtrsim 2$ so that we take the difference between the estimates to indicate a different interpretation of the physical system.

To sum up, we have obtained estimates for the sink strength of arrays of dislocation loops using cell models and a self-consistent scheme. We have compared the estimates from the appropriate cell model with the results from published numerical calculations. As only limited numerical results are available within the range of validity of our approximations, we have not been able to assess the usefulness of our results. The self-consistent scheme seems to us to offer the better approach to obtaining estimates for the sink strength at low concentrations of loops when the loop-defect interaction is weak. It is systematic and can handle the presence of other sinks; also, for a network of loops it includes the screening of opposite sides of a loop. Finally, there is no need to impose an artificial outer boundary, which, as we have seen, leads to a further restriction on the range of validity of our approximate solutions for the cell models by requiring $R_c/a \gg 1$.

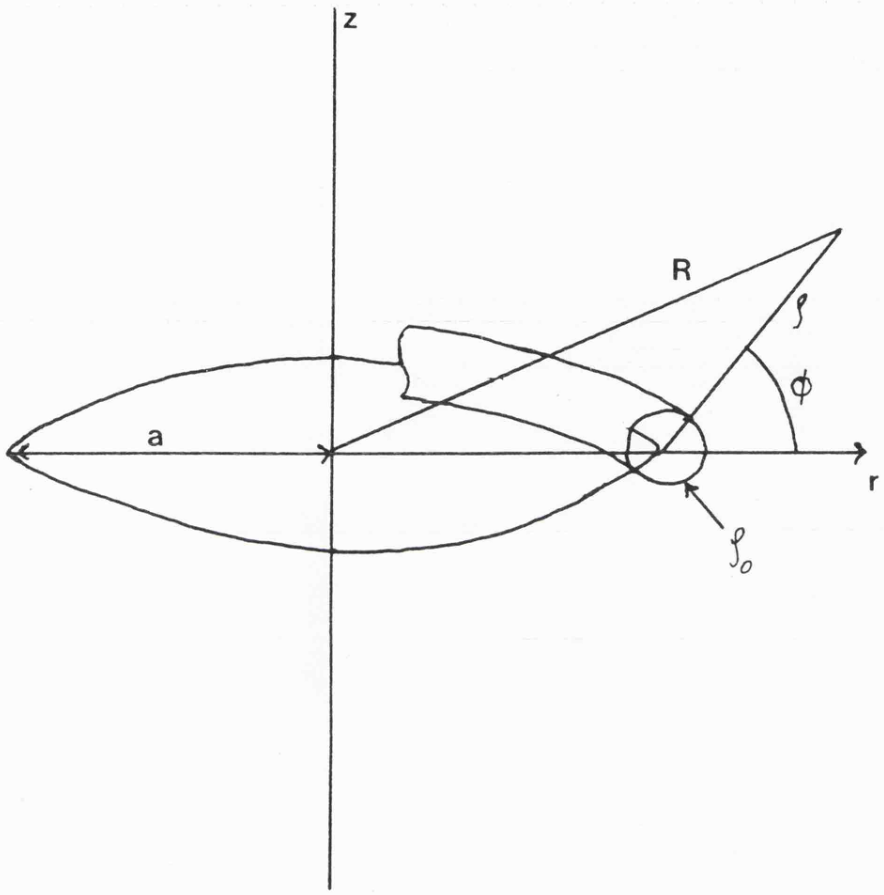


Figure 3.1 The loop core geometry.

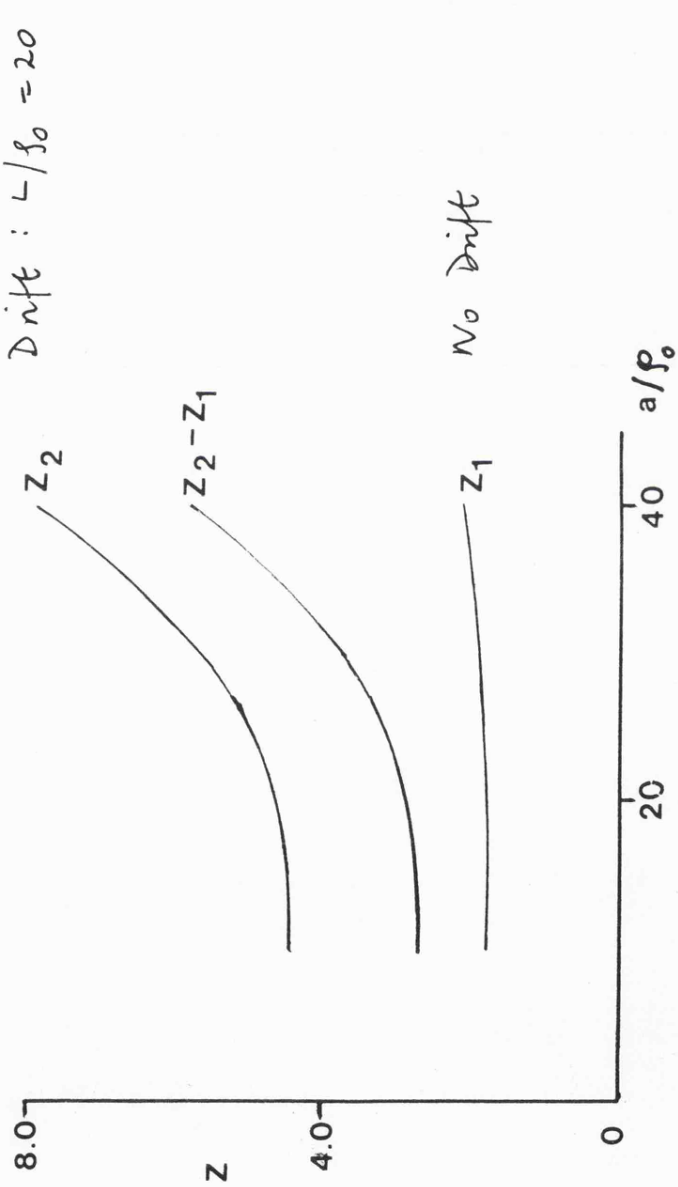


Figure 3.2 Estimates for Z using cell model with c = 1 on R = R_c with R_c/ρ_0 = 60.

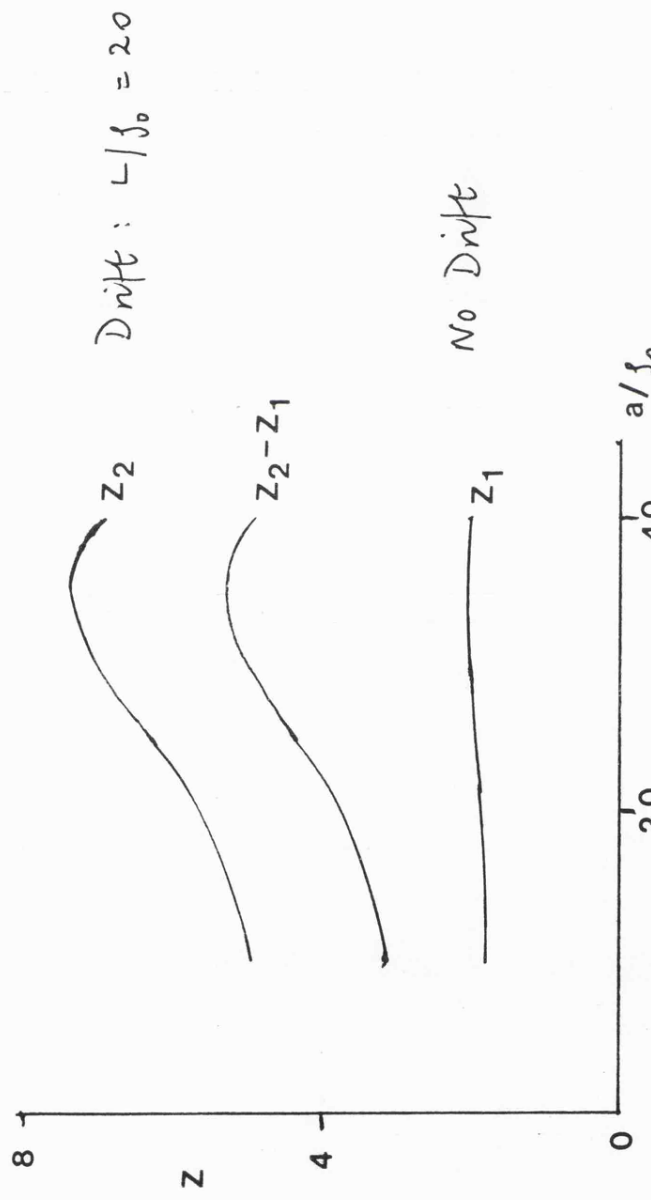


Figure 3.3 Estimates for Z using cell model with generation rate K with $R_c/\beta_0 = 60$.

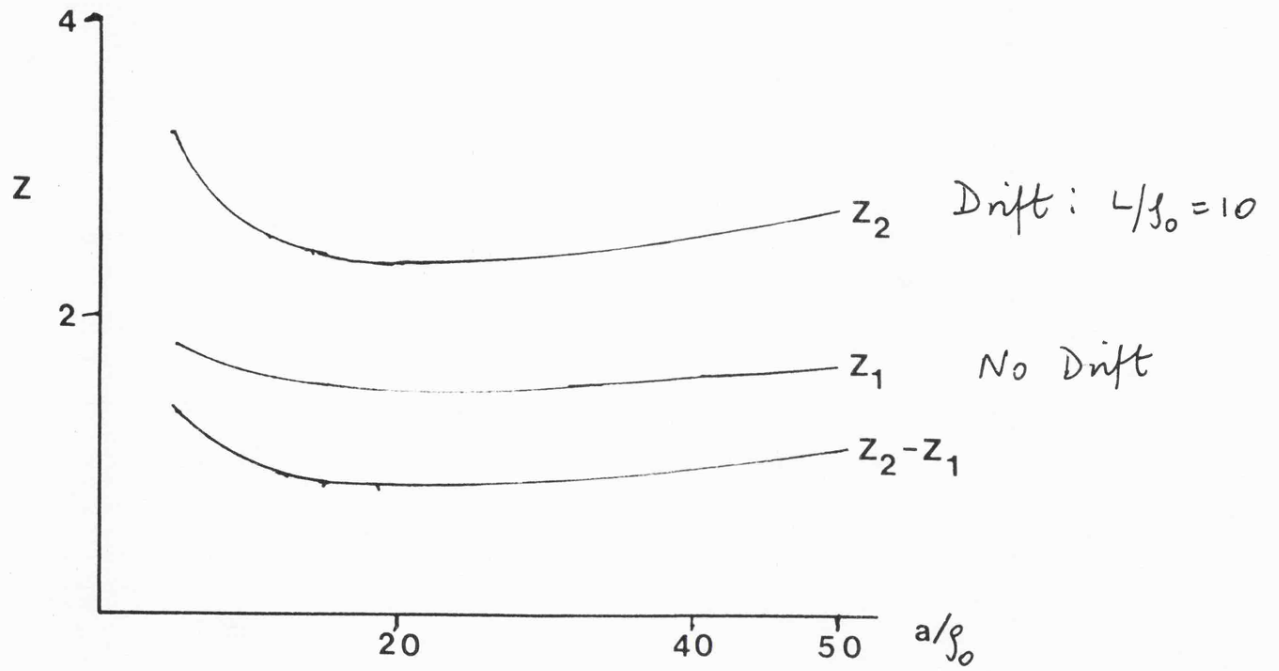


Figure 3.4 Estimates for Z using cell model with c = 1 on $R = R_c$ with $R_c/\ell_0 = 100$.

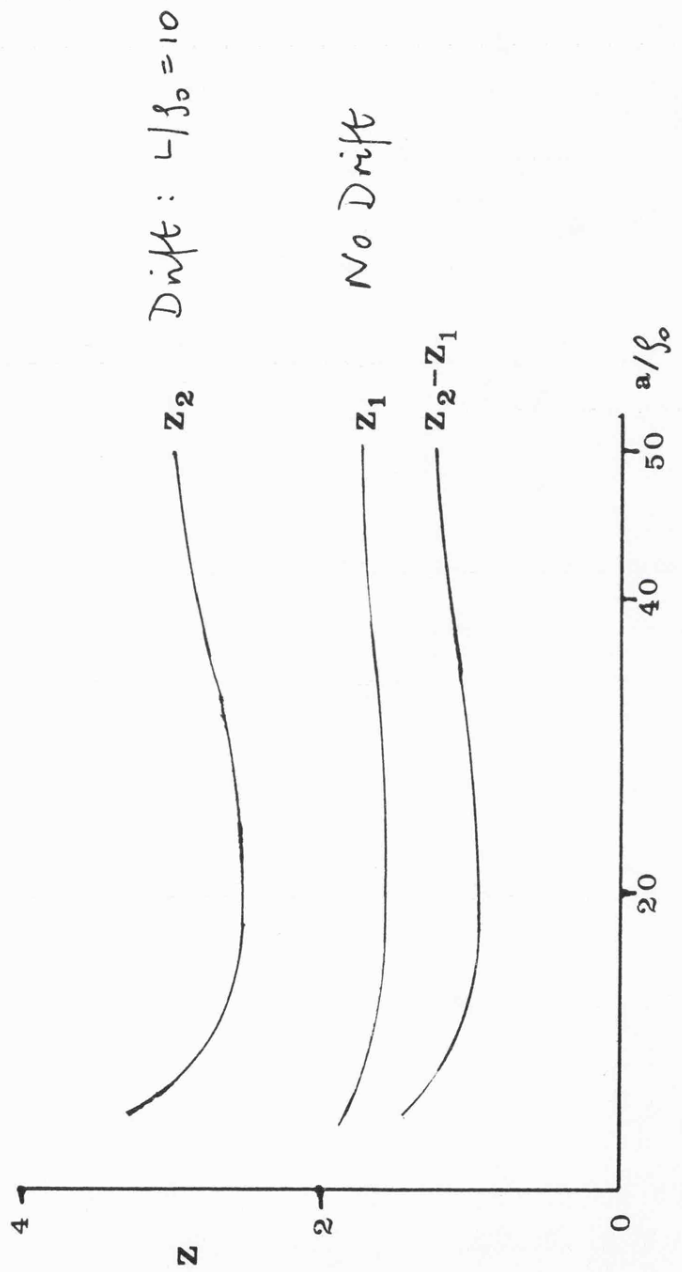


Figure 3.5 Estimates for Z using cell model with generation rate K with $R_c/\ell_0 = 100$.

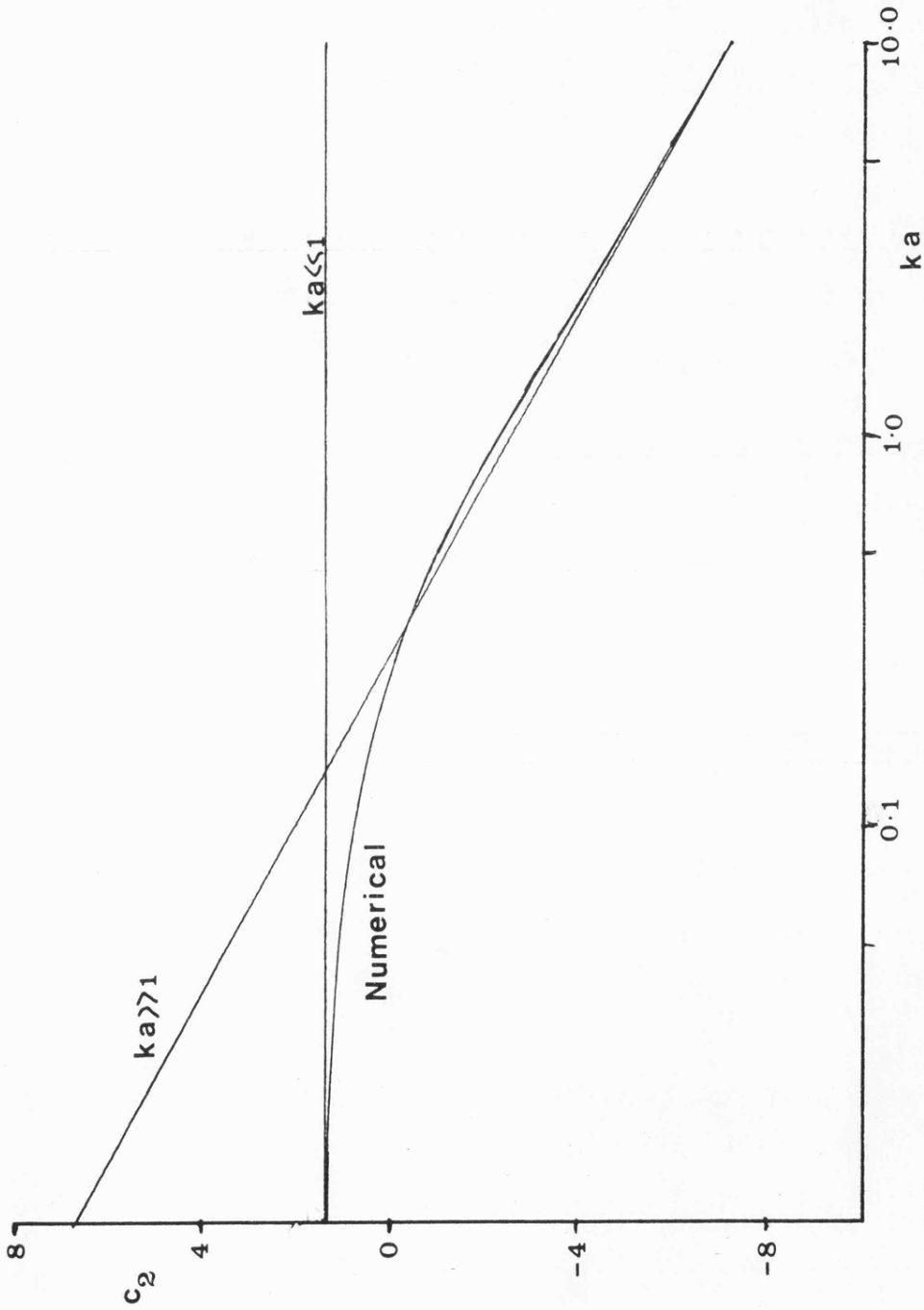


Figure 3.6 Plots of c_2 against ka for the approximations when ka $\ll$1, ka $\gg$1 together with numerical results.

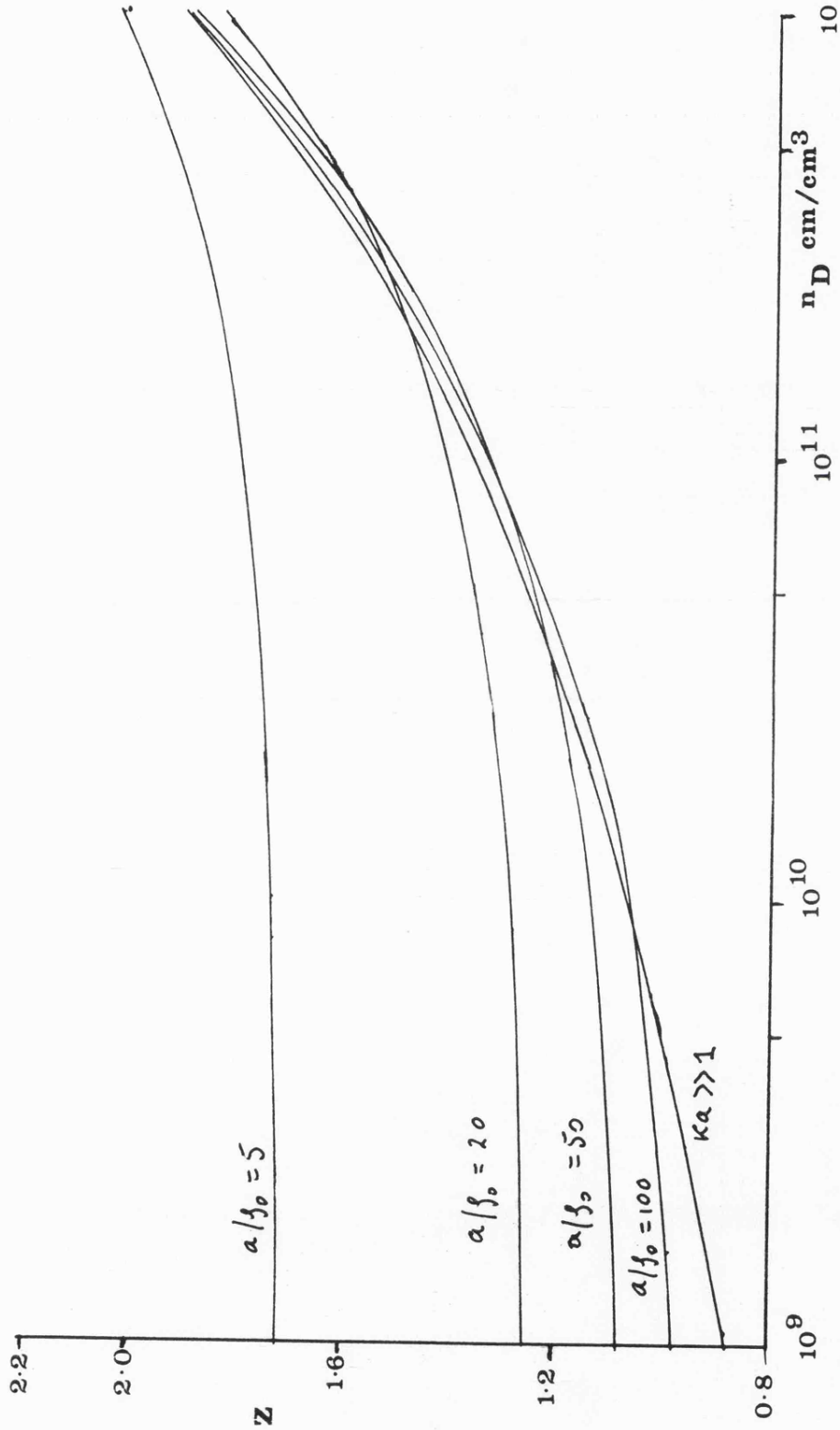


Figure 3.7 Self-consistent estimates for Z when there is no drift field, labelled by loop size.

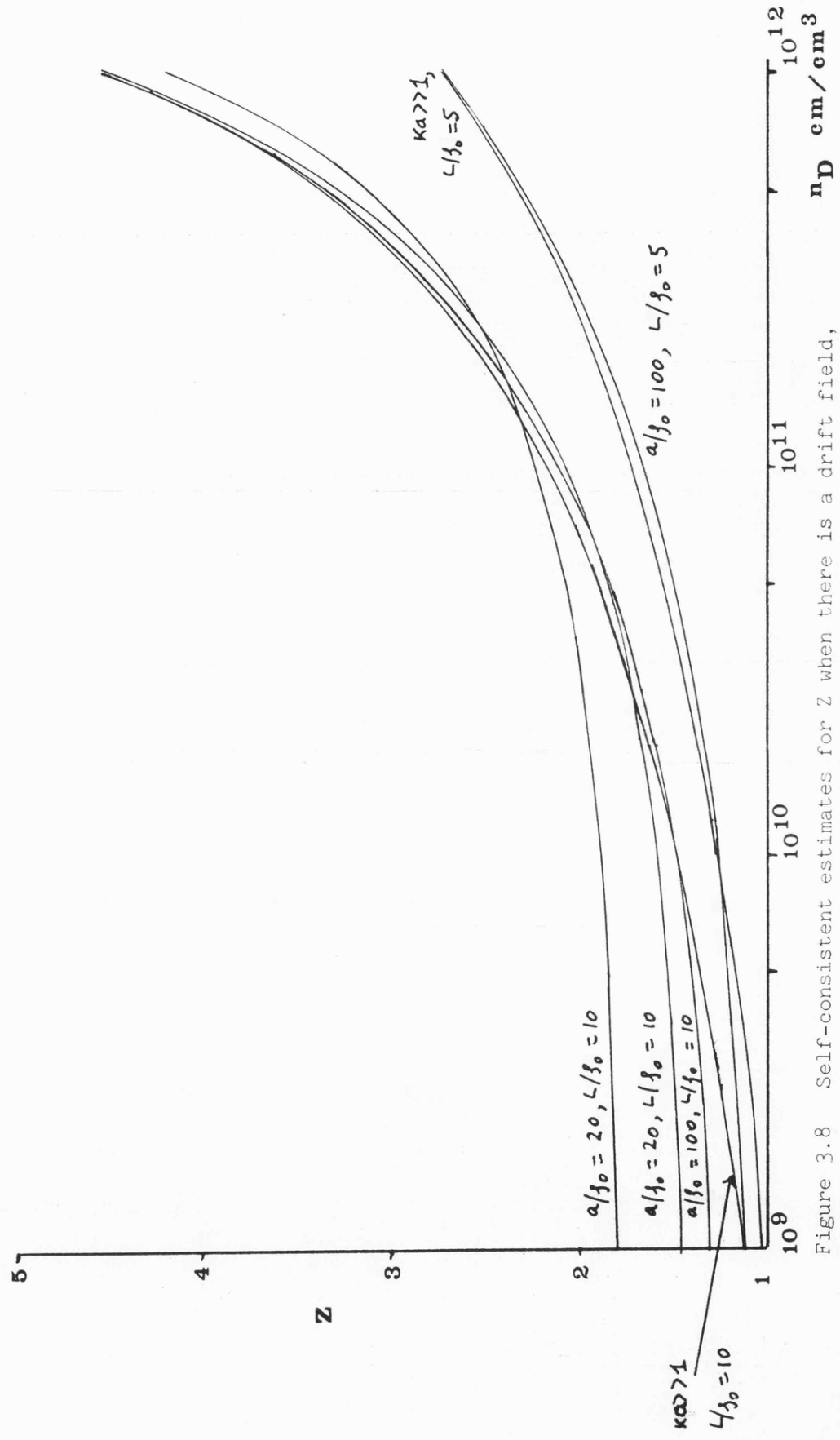


Figure 3.8 Self-consistent estimates for Z when there is a drift field, labelled by loop size and interaction length.

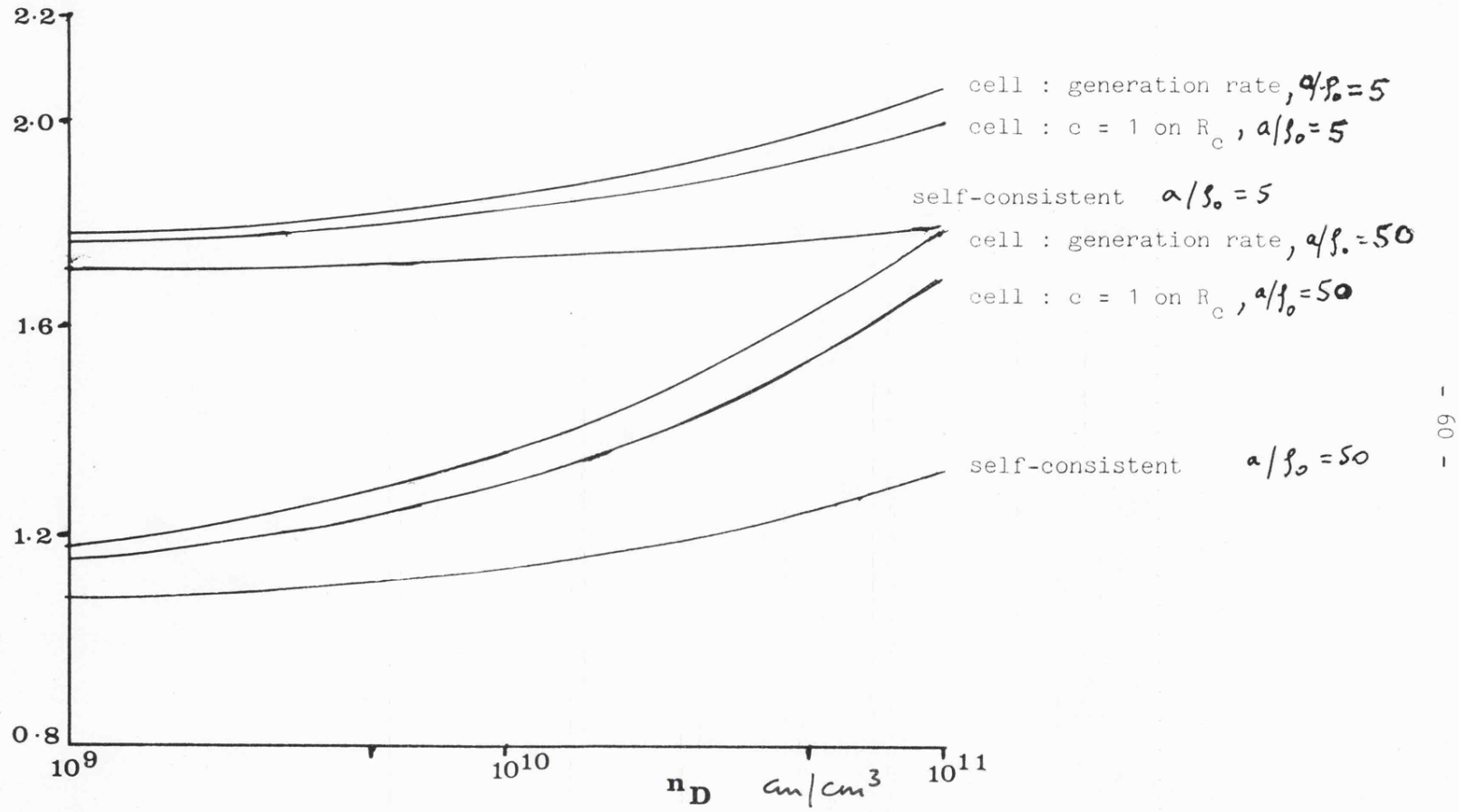


Figure 3.9 Comparison of cell models and self-consistent estimates with no drift.

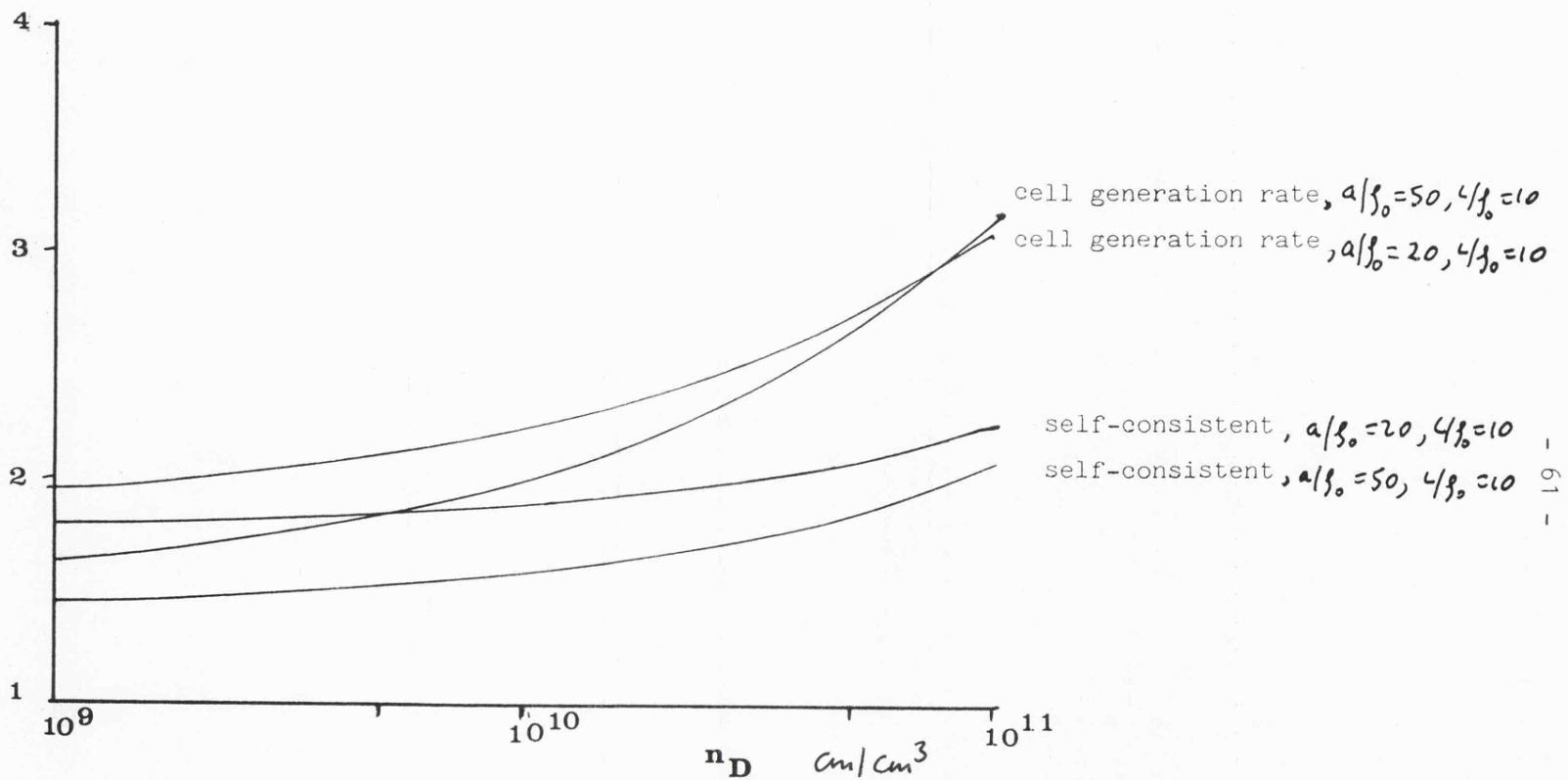


Figure 3.10 Comparison of cell models and self-consistent estimates with drift

4. The Effective Sink Strength of a Random Array of Voids.

4.1 Introduction

In the previous two chapters we have performed self-consistent calculations to provide estimates of the overall sink strength of arrays of loop and straight dislocations without being concerned about the validity of such a scheme. The calculations have also been complicated by the sink geometry or the presence of an interaction field. We now consider a simple model problem involving a distribution of spherical voids which act as sinks for a single diffusing population of defects. We will also assume that there is no energy of interaction between the defects and sinks. Our purpose now is to obtain more rigorous estimates of the sink strength of such an array than those obtained by self-consistent calculations.

We begin by formulating a problem exactly for a finite body containing a specified distribution of voids and give a precise definition of the effective sink strength of that distribution, analogous to the definition of the overall elastic moduli of a composite given by Hill (1952). We then give an integral equation formulation of the boundary value problem which is similar in form to that employed in the 'overall modulus' problem by Willis and Acton (1976) and Willis (1977, 1978). However, in contrast to the overall modulus problem, we have to make explicit allowance for boundary layer effects because it is impossible to secure integrals that are guaranteed to converge. Estimates of the sink strength will then be found from a variational principle. The derivation of the principle we give here is different from that given by Willis (1978) and Talbot and Willis (1980): we now start from a 'classical' variational principle and show that the principle given previously is obtained by neglecting a quadratic term. This is directly analogous to the derivation of the Hashin-Shtrikman principle from the classical energy principle of elastostatics given by Hill (1963) and to the derivation of variational principles for elastodynamics by Willis (1981a). We obtain lower bounds for the sink strength by substituting simple configuration-dependent trial fields into the variational functional, ensemble averaging and extremizing. Although we have to allow explicitly for the boundary of the finite body,

at this stage we can take the body to be large and obtain uniformity except in a boundary layer.

We can relate the results of the variational formulation to a perturbation expansion of the solution of the integral equation, similar to the one given by Brailsford (1976). We show that the simplest approximation derived from perturbation theory, which is strictly valid only at low concentrations, does in fact coincide with a strict lower bound, valid at any concentration. We demonstrate the extreme sensitivity of the bound to the statistics of the void distribution and show that as the self-consistent approximation lacks this sensitivity we can find pair correlation functions for which the rigorous lower bound exceeds the self-consistent estimate. We also show that the sensitivity of the bound is so marked that an apparent lower bound obtained using the 'well-stirred' approximation becomes infinite at a volume concentration of voids around 0.2 and thus provide evidence that this distribution is unrealizable at high concentration.

4.2 Formulation of the Model Problem and Self Consistent Calculation.

We consider a body occupying a region V, with boundary ∂V, containing exactly N spherical voids each of radius a centred at x_A (A=1,2...N). We denote the region occupied by voids V_v and assume that defects are introduced throughout $V \setminus V_v$ at a rate K(x,t) per unit volume. The defects distribute themselves by diffusion, so that their concentration c(x,t) satisfies the equation

$$\frac{\partial c}{\partial t} = D\nabla^2 c + K(x,t) , \quad x \in V \setminus V_v , \tag{4.2.1}$$

together with appropriate boundary conditions. If we assume there is no flux across ∂V, then

$$\frac{\partial c}{\partial n} = 0 , \quad x \in \partial V , \tag{4.2.2}$$

and the voids are the only sinks for the defects. We apply the simple boundary condition

$$c = 0 , \quad x \in \partial V_v , \tag{4.2.3}$$

on the void surfaces. The problem described by (4.2.1) to (4.2.3) is a complex one if N is large, even if possible growth of the voids is not admitted, and it is generally assumed that (4.2.1) and (4.2.3) can be replaced by a single 'homogenized' equation

$$\frac{\partial c}{\partial t} = \hat{D}\left(\nabla^2 c - \kappa^2 c\right) + \hat{K}(x,t), \quad x \in V, \tag{4.2.4}$$

in which $\hat{K}$ is some smoothed-out version of K (in a real situation K is unlikely to be known in any case), the distribution of voids is modelled by a continuous distribution of sinks of strength k^2 per unit volume and $\hat{D}$ is some 'overall' diffusion coefficient, usually (but perhaps incorrectly) identified with D. The outer boundary condition (4.2.2) is retained.

We make no attempt to justify replacement of (4.2.1) and (4.2.3) by (4.2.4) but remark however, that if the replacement is to succeed generally, it must do so under steady state conditions with K uniform throughout $V \setminus V_v$. Equation (4.2.2) then reduces to

$$-\nabla^2 c + K/D = 0, \tag{4.2.5}$$

and (4.2.4) becomes

$$\nabla^2 c - \kappa^2 c + \hat{K}/\hat{D} = 0, \tag{4.2.6}$$

where $\hat{K} = K(1-\eta)$, η representing the volume ratio occupied by the voids. Equation (4.2.6), with the boundary condition (4.2.2), has the solution

$$c = \bar{c} = \hat{K}/(\hat{D}\kappa^2). \tag{4.2.7}$$

Thus the problem reduces to calculating from the solution of (4.2.2), (4.2.3) and (4.2.5), the mean value $\bar{c}$ of c, defined by

$$\bar{c} = \frac{1}{V}\int_{V \setminus V_v} c \, dx, \tag{4.2.8}$$

where we have also used V to denote the volume of the region, to avoid excessive notation. We now impose the minimal requirement of consistency of (4.2.7) and (4.2.8) to obtain the relation

$$(\hat{D}k^2)\,\bar{c} = K(1-\eta), \tag{4.2.9}$$

which we take to define $(\hat{D}k^2)$.

Mathematically, the problem is closely related to that of determining the drag exerted by a set of fixed spheres in a viscous fluid: the concentration c is analogous to fluid velocity and the sink term $\hat{D}k^2 c$ in (4.2.4) to Darcy resistance. A complete description would require a proper estimate for $\hat{D}$ but we do not consider the problem of finding such an estimate here.

Before proceeding further with the system (4.2.2), (4.2.3) and (4.2.5) we obtain a self-consistent estimate for k^2, and hence $\hat{D}k^2$ when $\hat{D}$ is identified with D. As in Chapters 2 and 3 we embed one sink in a medium containing a continuous distribution of sinks, so that

$$\nabla^2 c - \kappa^2 c + \kappa^2 = 0, \quad |x|>a, \tag{4.2.10}$$

with c=0 when |x|=a and where the source has been normalized so that $\bar{c}=1$. The appropriate solution of (4.2.10) is

$$c = 1 - (a/r)\, e^{-\kappa(r-a)}, \tag{4.2.11}$$

where r=|x|, so that the flux (normalized so that $\hat{D}=1$) into the void is given by

$$F = 4\pi a\,(1+\kappa a). \tag{4.2.12}$$

If, now, the actual voids are distributed at number density n=N/V (so that $\eta = \frac{4}{3}\pi a^3 n$), the requirement of self-consistency generates the equation

$$\kappa^2 = n\bar{F} = 4\pi a n\,(1+\kappa a), \tag{4.2.13}$$

for k. The drawback of this method is that it only allows qualitatively for the distribution of the voids. We will now proceed to obtain more rigorous estimates of $(\hat{D}\ k^2)$ which make explicit allowance for this distribution.

4.3 An Integral Equation and Variational Formulation

We now express the problem defined by equation (4.2.5), together with the boundary conditions (4.2.2) and (4.2.3) in the form of an integral equation. We first define a Green function for the region V by the equations

$$\nabla^2 \varsigma(x,x') = \delta(x-x') - 1/V, \quad x \in V, \tag{4.3.1}$$

$$(\partial\varsigma/\partial n)(x,x') = 0, \quad x \in \partial V, \tag{4.3.2}$$

in which the right side of (4.3.1) satisfies the no net source condition required for consistency with (4.3.2). The solution of (4.3.1), (4.3.2) is made unique by requiring that

$$\int_V \varsigma(x,x')\,dx = 0 \tag{4.3.3}$$

which also ensures that G(x,x') = G(x',x). Application of Green's Theorem over the region $V \setminus V_v$ now gives

$$c(x') - \bar{c} = \int_{\partial V_v} \varsigma(x,x') q(x)\,ds - K' \int_{V \setminus V_v} \varsigma(x,x')\,dx, \quad x' \in V \setminus V_v, \tag{4.3.4}$$

where

$$q(x) = \partial c(x)/\partial n, \quad x \in \partial V_v, \tag{4.3.5}$$

and

$$K' = K/D. \tag{4.3.6}$$

The boundary condition (4.2.3) now yields the equation

$$\int_{\partial V_V} \zeta(x,x')\, q(x)\, ds - K' \int_{V \setminus V_V} \zeta(x,x')\, dx + \bar{c} = 0, \quad x' \in \partial V_V, \qquad (4.3.7)$$

in which for consistency

$$(V - V_V) K' = \int_{\partial V_V} q(x)\, ds. \qquad (4.3.8)$$

The problem is to find $\bar{c}$ given K' or, equivalently, because the problem is linear, to find K' given $\bar{c}$. With the latter interpretation, equation (4.3.7), together with (4.3.8) becomes an integral equation for $q(x')$. Before proceeding further, we note that, when $x' \in \partial V_V$, (4.3.4) defines a function $c(x')$ which is harmonic and therefore zero within V_V; thus the integral equation formulation has some similarity with Howells's (1974) formulation of the 'viscous drag' problem, in which the velocity field was defined to be zero throughout the volume occupied by the spheres. There is also a similarity with the Hashin-Shtrikman formulation of the 'overall modulus' problem, in which a 'polarized' homogeneous comparison material is employed: the field $c(x')$ of the present problem would be generated in a homogeneous medium if sinks $q(x)$ were introduced over ∂V_V. Thus the sinks $q(x)$ are in approximate correspondence with the 'polarization' and equation (4.3.7) corresponds to an integral equation for the polarization considered, for example, by Korringa (1973), Willis and Acton (1976) and Willis (1977).

Now, for any suitably smooth field c^*,

$$0 \leq \frac{1}{V} \int_{V \setminus V_V} (\nabla c - \nabla c^*)^2\, dx, \qquad (4.3.9)$$

and if c^* satisfies

$$\nabla^2 c^* + K^* = 0, \quad x \in V \setminus V_V, \qquad (4.3.10)$$

$$\nabla^2 c^* = 0, \quad x \in V_V, \qquad (4.3.11)$$

$$\partial c^* / \partial n = 0, \quad x \in \partial V, \qquad (4.3.12)$$

equation (4.3.9) can be rearranged using Gauss's theorem and the boundary conditions for c to get

$$0 \le K'\bar{c} - 2K^*\bar{c} + \frac{1}{V}\int_{V\setminus V_v} K^* c^* dx + \frac{1}{V}\int_{\partial V_v} c^* \frac{\partial c^*}{\partial n}\, ds. \qquad (4.3.13)$$

For any q* satisfying

$$K^* = \frac{1}{V(1-\eta)}\int_{\partial V_v} q^*(x)\, ds, \qquad (4.3.14)$$

c*, given by

$$c^*(x') = \bar{c}^* + \int_{\partial V_v} \zeta(x,x') q^*(x) ds + \int_{V_v} K^* \zeta(x,x')\, dx, \qquad (4.3.15)$$

is a solution of (4.3.10) to (4.3.12). We can interpret q* in (4.3.15) as the jump in $\partial c^*/\partial n$ across ∂V_v.

Next, the final integral in (4.3.13) can be written

$$\int_{\partial V_v} c^* \frac{\partial c^*}{\partial n}\, ds = -\int_{\partial V_v} c^* q^*\, ds - \int_{V_v} (\nabla c^*)^2 dx, \qquad (4.3.16)$$

so that substituting (4.3.15) into (4.3.13) with $\bar{c}^* = \bar{c}$ and making use of the mean value of G and (4.3.14) we find

$$0 \le K'\bar{c} - \frac{1}{V}\left\{\int_{\partial V_v} ds' q^*(x') + K^*\int_{V_v} dx'\right\}\left\{\int_{\partial V_v} ds\, \zeta(x,x') q^*(x) + K^*\int_{V_v} dx\, \zeta(x,x') + 2\bar{c}\right\} - \int_{V_v} (\nabla c^*)^2 dx. \qquad (4.3.17)$$

It is easy to show that for any q* the second term in (4.3.17) is negative so that this inequality implies the maximum principle

$$\frac{1}{V}\left\{\int_{\partial V_v} ds' q^*(x') + K^* \int_{V_v} dx'\right\}\left\{\int_{\partial V_v} ds\, \zeta(x,x') q^*(x) + K^* \int_{V_v} dx\, \zeta(x,x') + 2\bar{c}\right\} \leq K'\bar{c}. \tag{4.3.18}$$

The principle (4.3.18) was derived by Talbot and Willis (1980) directly from the integral equation and we now see that its status is analogous to that of the Hashin-Shtrikman principle in relation to the classical energy principle. This feature will reoccur in the context of another variational principle to be derived in Chapter 5.

The maximum principle (4.3.18) provides a ready source of precise information about the overall sink strength $\hat{D}k^2$: for any choice of q*, it generates a lower bound for K' and so, through (4.2.9), a strict lower bound to $\hat{D}k^2$.

Approximations q* will be considered in the sequel, which are constant over the surface of any sphere. If the region occupied by sphere A is denoted by V_A, with surface ∂V_A, q* will be taken to have the form

$$q^*(x) = q^A, \quad x \in \partial V_A, \quad A = 1,2,\ldots N, \tag{4.3.19}$$

where q^A (A=1,2,...N) are constants. Then (4.3.18) gives

$$\frac{1}{V}\sum_A{}' \left\{\int_{\partial V_A} ds' q^A + K^* \int_{V_A} dx'\right\}\left\{\int_{\partial V_A} ds\, \zeta(x,x') q^A + K^* \int_{V_A} dx\, \zeta(x,x')\right.$$

$$\left. + \sum_{B\neq A}{}' \left[\int_{\partial V_B} ds\, \zeta(x,x') q^B + K^* \int_{V_B} dx\, \zeta(x,x')\right] + 2\bar{c}\right\} \leq K'\bar{c}, \tag{4.3.20}$$

where

$$K^* = \frac{4\pi a^2}{V(1-\eta)} \sum_A{}' q^A. \tag{4.3.21}$$

Now when x' lies within V_A or else on its surface ∂V_A, and x is within V_B or on ∂V_B, G(x,x') can be expressed in the form

$$G(x,x') = -|x-x_B|^2/6V + G_1(x,x'), \tag{4.3.22}$$

for some function G_1 which is harmonic in x, with $G_1(x_B,x') = G(x_B,x')$. The mean value theorem therefore gives

$$\int_{\partial V_B} G(x,x')\,dS = 4\pi a^2 G(x_B,x') - 2\pi a^4/3V, \tag{4.3.23}$$

and

$$\int_{V_B} G(x,x')\,dx = \frac{4\pi a^3}{3} G(x_B,x') - 2\pi a^5/15V. \tag{4.3.24}$$

Also, when both x and x' are within or close to V_A,

$$G(x,x') = -\frac{1}{4\pi|x-x'|} - \frac{|x-x_A|^2}{6V} + G_A(x,x'), \tag{4.3.25}$$

for some function G_A which is harmonic in x, and it follows that

$$\int_{\partial V_A} G(x,x')\,dS = -a - \frac{2\pi a^4}{3V} + 4\pi a^2 G_A(x_A,x'), \quad x'\in V_A, \tag{4.3.26}$$

and

$$\int_{V_A} G(x,x')\,dx = -\frac{a^2}{2} + \frac{|x'-x_A|^2}{6} - \frac{2\pi a^5}{15V} + \frac{4\pi a^3}{3} G_A(x_A,x'), \quad x'\in V_A. \tag{4.3.27}$$

The results (4.3.23), (4.3.24), (4.3.26) and (4.3.27) may be substituted into (4.3.20) and then used again to reduce the integrals over x' (remembering that $G_A(x_A,x')$ is not harmonic in x' but instead has a representation like (4.3.25)). Use of (4.3.21), together with the relation $\eta = 4\pi a^3 N/3V$, leads finally to the inequality

$$\frac{1}{V}\sum_{A}{}'\left(4\pi a^2 q^A+\frac{4}{3}\pi a^3 K^*\right)\left[\left(\frac{-a+4\pi a^2\zeta_{AA}}{4\pi a^2}\right)\left(4\pi a^2 q^A+\frac{4}{3}\pi a^3 K^*\right)\right.$$

$$\left.+\sum_{B\neq A}\zeta_{AB}\left(4\pi a^2 q^B+\frac{4}{3}\pi a^3 K^*\right)\right]-\frac{a^2}{15}(5-\eta)(K^*)^2+2K^*\bar{c}$$

$$\leq K'\bar{c}, \qquad (4.3.28)$$

where G_A here denotes $G_A(x_A,x_A)$ and G_{AB} denotes $G(x_A,x_B)$. We will develop from (4.3.28) explicit bounds for K', valid when V is large and the voids are located only stochastically, in the following sections.

4.4 Description of the Random Medium

If the position of the N voids were known with precision (for example, if they were distributed on a lattice), the inequality (4.3.28) could be used immediately to provide a bound for K' which, furthermore, could be optimized by allowing the N constants q^A to vary. Although the particular problem studied here has not been analysed for periodic arrays of voids there is an extensive literature on homogenization for similar problems (see, for example, Bensoussan et al. (1978)). We now focus on a class of media in which the voids are distributed randomly, in a sense described informally below. The actual medium (for which, of course, the precise location of every void could be determined) is regarded as one taken from an ensemble of media, labelled by some parameter α from a sample space $\mathcal{S}$ over which a probability density $P(\alpha)$ is defined. The probability density P_A for finding a void centred at x_A is then defined from the requirement that, for any subset U of V, the expected number of voids centred in U is $\int_U P_A dx_A$. Thus,

$$\int_U P_A\,dx_A=\sum_{\kappa=1}^{N}\kappa\int_{\mathcal{S}_{U(\kappa)}}P(\alpha)\,d\alpha, \qquad (4.4.1)$$

where $\mathcal{S}_{U(k)}$ represents the subset of $\mathcal{S}$ for which there are exactly k voids centred in U. Since, plainly, $\mathcal{S}_{V(k)} = \mathcal{S}$ if k=N and is empty otherwise, equation (4.4.1) implies

$$\int_V \rho_A \, dx_A = N, \tag{4.4.2}$$

as it should. Similarly the joint probability density P_{AB} for finding distinct voids centred at x_A and x_B is defined so that, for disjoint subsets U and W of V, the expected value of the product of the number of voids centred in U with the number centred in W is

$$\int_U dx_A \int_W dx_B \, \rho_{AB};$$

thus

$$\int_U dx_A \int_W dx_B = \sum_{k=1}^{N-1} \sum_{\ell=1}^{N-k} k\ell \int_{\mathcal{S}_{U(k)W(\ell)}} P(\alpha) \, d\alpha, \tag{4.4.3}$$

where $\mathcal{S}_{U(k)W(\ell)}$ is the subset of $\mathcal{S}$ for which there are k voids in U and ℓ in W. If U is so small that it can contain at most one void, and if $W=V\setminus U$, then $\mathcal{S}_{U(k)W(\ell)} = \mathcal{S}_{U(k)}$ if $\ell = N-K$ and k=0 or 1 and is empty otherwise. In this case therefore

$$\int_U dx_A \int_W dx_B \, \rho_{AB} = (N-1) \int_{\mathcal{S}_{U(K)}} P(\alpha) \, d\alpha = (N-1) \int_U \rho_A \, dx_A. \tag{4.4.4}$$

If the conditional density $P_{B|A}$ is now defined by the relation

$$\rho_{AB} = \rho_{B|A} \, \rho_A, \tag{4.4.5}$$

(with $P_{A|A}=0$), equation (4.4.4) implies

$$\int_V \rho_{B|A} \, dx_B = (N-1), \tag{4.4.6}$$

which states that if there is a void at x_A, then there must be exactly N-1 others in V. Higher order densities are defined similarly : $P_{ABCD...}$ will denote the joint probability density for finding voids centred at x_A, x_B, x_C, x_D..., and $P_{AB...\ CD...}$ will denote the joint probability density for finding voids centred at x_A, x_B..., given that voids are centred at x_C, x_D.... For either, the voids are always assumed distinct, so that a repeated suffix will always imply that the density is zero.

We have assumed implicitly in the above that the voids cannot overlap, that is, the model is of the 'hard-core' type. Otherwise, the description is fairly general. For the work to follow, however, some further assumptions will be made. First, the limiting case of a large region V will be considered, with the number density n=N/V remaining finite. Also, in this limit, we will assume that the distribution of voids is statistically uniform in the sense that $P_{AB...}$ is insensitive to rigid translations of the points x_A, x_B..., except when one or more of the points is close to V. and statistically isotropic, in the sense that $P_{AB...}$ is insensitive to rigid rotations of x_A, x_B..., again except when some point is close to ∂V. This implies, in particular, that $P_A \sim n$ except when x_A is close to ∂V. We will further assume that there is no long-range order in the sense that

$$P_{AB...CD...} \sim P_{AB...} P_{CD...} , \qquad (4.4.7)$$

when the points (x_A, x_B ...) are far from the points (x_C, x_D ...) even when some points may be close to ∂V. Exact conditions under which a process for generating a random medium realizes the above assumptions are unknown. Also, it will emerge later that some initially plausible functions P_{AB} generate results that are untenable and so presumably cannot be realized for any hard-core model. Again, however, systematic necessary restrictions are not yet known.

4.5 A Simple Lower Bound for K'

Given a particular realization of the random medium with parameter α, the position of each void is specified and solving the integral equation (4.3.7) would yield a value $K'(\alpha)$ for K', which would depend on α. It seems plausible, however, that, if V is large

and the medium correspondingly statistically uniform, $K'(\alpha)$ should become asymptotically independent of α, and so coincide with its expectation value

$$\langle K' \rangle = \int_{\mathcal{P}} K(\alpha) P(\alpha) \, d\alpha. \qquad (4.5.1)$$

Dually, if we calculate K' for a finite region V, then we might expect K' to tend to a well-defined limit as V becomes large. The object of this section will be to develop a simple lower bound for K', in the limit of large V. The bound is obtained by allowing q^A in the inequality (4.3.28) to depend just upon the position x_A of the sphere A, taking expectations of (4.3.28) and then optimizing the function $q^A = q^A(x_A)$. In view of the assumed statistical uniformity, it might be expected that the optimal q^A should be a constant q^0, independent of x_A. This will indeed be borne out in what follows, except when x_A is close to ∂V. It will appear, however, that substitution of $q^A = q^0$ directly into (4.3.28) even in the boundary layer leads to a useful answer only if the joint probability P_{AB} has some special (and generally implausible) properties, the Green function being sufficiently badly behaved for the contribution from the boundary layer to render the bound useless in the general case. This contrasts with the situation in 'overall modulus' theory, in which a piecewise constant polarization can be substituted directly into the variational principle analogous to (4.3.28), with negligible perturbation from the boundary layer when V is large (Willis (1977)). We note in passing that the bound we will obtain is not the best that can be found. Use of the inequality (4.3.17), would lead to an improved bound but would also generate expressions involving third order probability densities about which little or no information is available.

Proceeding now to details, the expectation value of the left side of (4.3.28) is maximized by setting its variation with respect to q^R equal to zero. It is easy to show, in fact, that the variation can be obtained by differentiating the left side of (4.3.28) with respect to q^R and then taking the conditional expectation, with x_R fixed. Taking account of the definition (4.3.21) for K^* and the symmetry of G_{AB}, the required derivative

is readily found to be (2/V) times the following expression:

$$4\pi a^2 \left\{ \left(\frac{-a + 4\pi a^2 \rho_R}{4\pi a^2} \right) \left(4\pi a^2 q^R + \frac{4}{3}\pi a^3 K^* \right) + \sum_{B \neq R}{}' \rho_{RB} \left(4\pi a^2 q^B + \frac{4}{3}\pi a^3 K^* \right) \right\}$$

$$+ \left(\frac{4}{3}\pi a^3 \right) \left(\frac{4\pi a^2}{V(1-\eta)} \right) \sum_A{}' \left\{ \left(\frac{-a + 4\pi a^2 \rho_A}{4\pi a^2} \right) \left(4\pi a^2 q^A + \frac{4}{3}\pi a^3 K^* \right) \right.$$

$$\left. + \sum_{B \neq A}{}' \rho_{AB} \left(4\pi a^2 q^B + \frac{4}{3}\pi a^3 K^* \right) \right\} - \frac{4\pi a^4 (5-\eta)}{15(1-\eta)} + \frac{4\pi a^2}{1-\eta} \bar{c}. \tag{4.5.2}$$

Taking the expectation value with x_R fixed is a little complicated because the suffix R must be removed explicitly from every summation. Anticipating the form of the final result when V is large, however, the expression is much simplified if the conditional expectation of any mean value (that is, 1/V times a summation) is taken to coincide with its unconditional expectation value. Then, if we set

$$\phi_R = \left(\frac{-a + 4\pi a^2 \rho_R}{4\pi a^2} \right) \left(4\pi a^2 q^R + \frac{4}{3}\pi a^3 \langle K^* \rangle \right)$$

$$+ \int \rho_{RB} \rho_{BIR} \left(4\pi a^2 q^B + \frac{4}{3}\pi a^3 \langle K^* \rangle \right) dx_B, \tag{4.5.3}$$

where $\langle K^* \rangle$ denotes the unconditional expectation value of K*, the conditional expectation of (4.5.2) approximates to

$$4\pi a^2 \phi_R + \frac{4}{3}\pi a^3 \frac{4\pi a^2}{V(1-\eta)} \int \phi_A \rho_A dx_A - \frac{4\pi a^4 (5-\eta)}{15(1-\eta)} \langle K^* \rangle$$

$$+ \frac{4\pi a^2}{1-\eta} \bar{c}. \tag{4.5.4}$$

Setting this to zero shows that ϕ_R is independent of R so that the integral in (4.5.4) can be evaluated using (4.4.2). Use of the relation $\eta = 4\pi a^3 N/3V$ now gives the simple equation

$$\phi_R - \frac{1}{15} a^2 (5-\eta)\langle K^* \rangle + \bar{c} = 0, \tag{4.5.5}$$

To proceed further, we set

$$q^A = (1-\eta) a \langle K^* \rangle / 3\eta + e^A, \tag{4.5.6}$$

where

$$\int e^A P_A \, dx_A = 0, \tag{4.5.7}$$

consistently with (4.3.21). Equation (4.5.5) may now be written in the form

$$\left(\frac{a\langle K^* \rangle}{3\eta}\right)\left\{(-a + 4\pi a^2 \zeta_R) + 4\pi a^2 \int \zeta_{RB} P_{B|R} \, dx_B \right\}$$

$$+ e^R(-a + 4\pi a^2 \zeta_R) + 4\pi a^2 \int \zeta_{RB} P_{B|R} e^B dx_B - \frac{1}{15} a^2 (5-\eta)\langle K^* \rangle + \bar{c}$$

$$= 0, \tag{4.5.8}$$

or, regrouping terms,

$$(-a + 4\pi a^2 \zeta_R)\left(\frac{a}{3\eta}\langle K^* \rangle + e^R\right) + 4\pi a^2 \int \zeta_{RB}\left(\frac{a}{3\eta}\langle K^* \rangle + e^B\right)(P_{B|R} - P_B) dx_B$$

$$+ 4\pi a^2 \int \zeta_{RB}\left(\frac{a}{3\eta}\langle K^* \rangle (P_B - n) + e^B P_B\right) dx_B - \frac{1}{15} a^2 (5-\eta)\langle K^* \rangle + \bar{c} = 0, \tag{4.5.9}$$

having also used that G has zero mean value to replace P_B by $(P_B - n)$. The assumption of no long range order ensures (with some restriction on the rate of decay of $P_{B|R} - P_B$) that the first integral in (4.5.9) remains finite as V becomes large. Therefore,

except when x_R is close to ∂V (when G_R may be large), the second integral must be finite : this implies

$$(a/3\eta)\langle K^*\rangle(\rho_B - n) + e^B \rho_B \sim 0 , \qquad (4.5.10)$$

except, perhaps, when x_B lies in a boundary layer close to ∂V, across which the left side of (4.5.10) should have a small mean value. Since $P_B - n \sim 0$ except in the boundary layer, it follows that $e^B \sim 0$ so that q^B is constant except close to ∂V. Then, when x_R is not in the boundary layer, equation (4.5.9) simplifies to

$$\frac{a}{3\eta}\langle K^*\rangle\left\{-a + 4\pi a^2 \int \zeta_{RB}(\rho_{B|R} - \rho_B)\,dx_B\right\} - \frac{1}{15}a^2(5-\eta)\langle K^*\rangle + \bar{c}$$

$$+ 4\pi a^2 \int \zeta_{RB}\left[\frac{a}{3\eta}\langle K^*\rangle(\rho_B - n) + e^B \rho_B\right] dx_B = 0, \qquad (4.5.11)$$

since $G_R \sim 0$ and $e^R \sim 0$. When V is large, the first integral in (4.5.11) is independent of x_R because $(P_{B|R} - P_B)$ is insensitive to translations and, because the integral converges G_{RB} may be replaced by its infinite body form

$$\zeta_{RB} \sim -\frac{1}{4\pi|x_B - x_R|} \qquad (4.5.12)$$

Hence , the last integral is not only finite but independent of x_R and therefore zero, since its mean value over x_R is zero, by (4.3.3). Hence, finally, the equation

$$\frac{a^2}{3\eta}\langle K^*\rangle\left\{1 + a\int \frac{\rho_{B|R} - \rho_B}{|x_B - x_R|}\,dx_B + \frac{1}{5}\eta(5-\eta)\right\} = \bar{c}, \qquad (4.5.13)$$

defines $\langle K^*\rangle$ as a lower bound for $\langle K'\rangle$.

It should be noted that, if q^A had been taken independent of x_A from the outset, the terms involving e^B would have been absent from (4.5.9) and that equation would have been dominated by the term

$$4\pi a^2\left(\tfrac{1}{3}a\langle K^*\rangle\right)\int \zeta_{RB}(\rho_B - n)\,dx_B . \qquad (4.5.14)$$

It is quite conceivable that, close to ∂V, P_B might differ greatly from n : for instance, it might be exactly zero. Then since G_{RB} would be of the order d^{-1}, where d is a typical diameter of V, the term (4.5.14) would be of order d times the thickness of the boundary layer and so would become indefinitely large with V. This point was overlooked in an earlier derivation of (4.5.13) by Willis (1978), whose reasoning was strictly valid only for a special class of distributions P_B.

We have, in fact, performed an exact reduction of (4.5.2), but the calculations are laborious and lead to modifications to (4.5.9) that are only significant in the boundary layer. The term highlighted in equation (4.5.10) remains the dominant feature, and (4.5.13) survives unchanged.

4.6 Pairwise Interactions

We now look for an improved lower bound for K' by adopting the form

$$q^A = r^A + \sum_{B \neq A}{}' f^{AB} \qquad (4.6.1)$$

for q^A in (4.3.28), which allows for pairwise interactions. In (4.6.1), r^A depends upon x_A and f^{AB} depends upon both x_A and x_B. Clearly for any given q^A, the resolution (4.6.1) is not unique but in the limit of large V, it can be made to be by requiring that $f^{AB} \to 0$ as $|x_B - x_A| \to \infty$. For finite V, there is no objection to substituting (4.6.1) in (4.3.28) and optimizing; there will simply be no unique maximizer unless further conditions are imposed. Following the scheme outlined in the last section, we substitute (4.6.1) in (4.3.28) and optimize the expected value of the result. The required variational equations are obtained by differentiating with respect to r^R and taking the expectation of the result conditional upon x_R being fixed, and differentiating with respect to f^{RS} and taking the expectation of the result with x_R and x_S fixed. Now from (4.6.1)

$$\frac{\partial q^A}{\partial r^R} = \frac{\partial q^A}{\partial f^{RS}} = \delta_{AR}. \qquad (4.6.2)$$

Also, from (4.3.21)

$$K^* = \frac{4\pi a^2}{V(1-\eta)} \sum_A' \left[r^A + \sum_{B\neq A}' f^{AB} \right], \tag{4.6.3}$$

so that

$$\frac{\partial K^*}{\partial r^R} = \frac{\partial K^*}{\partial f^{RS}} = \frac{4\pi a^2}{V(1-\eta)}. \tag{4.6.4}$$

It follows, therefore, that the derivative of the left side of (4.3.28) with respect to either r^R or f^{RS} is 2/V times

$$\sum_A' \left(4\pi a^2 \delta_{AR} + \frac{4\pi a^3}{3} \frac{4\pi a^2}{V(1-\eta)}\right) \left\{ (-a + 4\pi a^2 \zeta_A)\left(r^A + \sum_{B\neq A}' f^{AB} + \frac{1}{3} a K^*\right) \right.$$

$$\left. + 4\pi a^2 \sum_{B\neq A}' \zeta_{AB} \left(r^B + \sum_{C\neq B}' f^{BC} + \frac{a}{3} K^*\right) \right\} - \frac{a^2(5-\eta)}{15(1-\eta)} K^* + \frac{\bar{c}}{(1-\eta)}, \tag{4.6.5}$$

whose conditional expectation keeping x_R fixed gives the variation with respect to r^R, while the variation with respect to f^{RS} is obtained by keeping x_R and x_S fixed. Again, as in § 5 great simplification is achieved if conditional expectations of mean values are replaced directly by their unconditional expectation values. Then, if we define

$$\phi_R = (-a + 4\pi a^2 \zeta_R)\left(r^R + \frac{a}{3}\langle K^*\rangle + \int \rho_{B|R} f^{RB} dx_B\right)$$

$$+ 4\pi a^2 \int \rho_{B|R} \zeta_{RB} \left(r^B + f^{BR} + \frac{a}{3}\langle K^*\rangle\right) dx_B$$

$$+ 4\pi a^2 \iint \rho_{BC|R} \zeta_{RB} f^{BC} dx_B dx_C, \tag{4.6.6}$$

and

$$\psi_{RS} = (-a^2 + 4\pi a^2 \varrho_R)\left(r^R + \frac{a}{3}\langle\kappa^*\rangle + f^{RS} + \int f^{RB} P_{B|R}\, dx_B\right)$$
$$+ 4\pi a^2 \varrho_{RS}\left(r^S + \frac{a}{3}\langle\kappa^*\rangle + f^{SR} + \int f^{SC} P_{C|RS}\, dx_C\right)$$
$$+ 4\pi a^2 \int \varrho_{RB}\left(r^B + \frac{a}{3}\langle\kappa^*\rangle + f^{RB} + f^{BS}\right) P_{B|RS}\, dx_B$$
$$+ 4\pi a^2 \iint \varrho_{RB} f^{BC} P_{BC|RS}\, dx_B\, dx_C, \tag{4.6.7}$$

considering the variation with respect to r^R gives

$$\phi_R + \frac{4}{3}\pi a^3 \frac{1}{V(1-\eta)} \int \phi_A P_A\, dx_A - \frac{a^2(5-\eta)\langle\kappa^*\rangle}{15(1-\eta)} + \frac{\bar{c}}{1-\eta} = 0, \tag{4.6.8}$$

while considering the variation with respect to f^{RS} gives

$$\psi_{RS} + \frac{4}{3}\pi a^3 \frac{1}{V(1-\eta)} \int P_A \phi_A\, dx_A - \frac{a^2(5-\eta)\langle\kappa^*\rangle}{15(1-\eta)} + \frac{\bar{c}}{1-\eta} = 0. \tag{4.6.9}$$

Equation (4.6.8) has exactly the form of (4.5.4) and it follows that the new ϕ_R still satisfies (4.5.5). Equation (4.6.9) now implies that

$$\psi_{RS} = \phi_R = \frac{1}{15} a^2(5-\eta)\langle\kappa^*\rangle - \bar{c}, \tag{4.6.10}$$

so that both are independent of their arguments. Analogously to (4.5.6), we now set

$$r^A + \int f^{AB} P_{B|A}\, dx_B = \frac{(1-\eta)}{3\eta} a\langle\kappa^*\rangle + e^A, \tag{4.6.11}$$

so that e^A still satisfies (4.5.7). The equation for ϕ_R gives, after rearrangement,

$$(-a + 4\pi a^2 \varrho_R)\left[(a/3\eta)\langle\kappa^*\rangle + e^R\right] - \frac{1}{15} a^2(5-\eta)\langle\kappa^*\rangle + \bar{c}$$
$$+ 4\pi a^2 \int \varrho_{RB}\left[\{(a/3\eta)\langle\kappa^*\rangle + e^B\}(P_{B|R} - P_B) + f^{RB} P_{B|R}\right] dx_B$$
$$+ 4\pi a^2 \iint \varrho_{RB} f^{BC}(P_{BC|R} - P_{B|R} P_{C|B})\, dx_B\, dx_C$$
$$+ 4\pi a^2 \int \varrho_{RB}\left[(a/3\eta)\langle\kappa^*\rangle(P_B - n) + e^B P_B\right] dx_B = 0. \tag{4.6.12}$$

If V is taken large and it is assumed that $f^{BC} \to 0$ as $|x_B - x_C| \to \infty$ and that the voids have no long-range order, it follows, as in §5, that e^B is small except in a boundary layer close to ∂V and finally we conclude that, except when x_R is close to ∂V,

$$(a^2/3\eta)\langle K^* \rangle \left\{ 1 - 4\pi a \int \varsigma_{RB} (p_{B|R} - p_B) dx_B + \tfrac{1}{5}\eta(5-\eta) \right\}$$

$$- 4\pi a^2 \int \varsigma_{RB} f^{RB} p_{B|R} dx_B - 4\pi a^2 \iint \varsigma_{RB} f^{BC} (p_{BC|R} - p_{B|R} p_{C|B}) dx_B dx_C$$

$$= \bar{c}. \qquad (4.6.13)$$

The integrals involving f converge so long as f^{RB} tends to zero appropriately as $|x_B - x_R| \to \infty$. The other deduction we can make from (4.6.10) is that $\psi_{RS} - \phi_R = 0$. Explicitly, when x_R and x_S are not close to ∂V, this reduces to

$$- a \left(f^{RS} + \int f^{RB} (p_{B|RS} - p_{B|R}) dx_B \right)$$

$$+ 4\pi a^2 \varsigma_{RS} \left\{ (a/3\eta)\langle K^* \rangle + f^{SR} + \int f^{SC} (p_{C|RS} - p_{C|S}) dx_C \right\}$$

$$+ 4\pi a^2 \int \varsigma_{RB} \left[\left\{ (a/3\eta)\langle K^* \rangle + f^{BR} \right\} (p_{B|RS} - p_{B|R}) + f^{BS} p_{B|RS} \right] dx_B$$

$$+ 4\pi a^2 \iint \varsigma_{RB} f^{BC} (p_{BC|RS} - p_{BC|R} - p_{B|RS} p_{C|B} + p_{B|R} p_{C|B}) dx_B dx_C$$

$$= 0. \qquad (4.6.14)$$

This equation, although of some theoretical interest, is of little practical use because it involves correlations of up to four voids which will be unknown in practice. It is possible, however, to obtain an approximate solution valid at low concentrations of voids, by retaining only terms of zeroth order in the number density n. This eliminates the double integral, and also terms involving $P_{B|RS} - P_{B|R}$, since such integrands are 'short-range' and

the integrals converge with no assistance from f itself. The one integral that does not have this feature is retained, to give

$$-a f^{RS} + 4\pi a^2 \zeta_{RS} f^{SR} + (4\pi a^3/3\eta) \langle K^* \rangle \zeta_{RS} + 4\pi a^2 \int \zeta_{RS} f^{BS} \rho_B \, dx_B \sim 0, \tag{4.6.15}$$

the error committed by replacing $P_{B|RS}$ by P_B being of order n. When $|x_R - x_S| \gg a$, the term $4\pi a^2 G_{RS} f^{SR}$ may be dropped and then, taking the Laplacian of (4.6.15), it follows that

$$-a\nabla^2 f^{RS} + 4\pi a^2 n f^{RS} = -(4\pi a^3/3\eta) \langle K^* \rangle \delta(x_R - x_S), \tag{4.6.16}$$

since $P_B \sim n$. The right side of (4.6.16) is, of course, only a formal approximation. Equation (4.6.16) has the solution

$$f^{RS} = -\frac{a^2}{3} \langle K^* \rangle \frac{\exp(-\beta |x_R - x_S|)}{|x_R - x_S|}, \tag{4.6.17}$$

where

$$\beta^2 = 4\pi a n. \tag{4.6.18}$$

Although this analysis is approximate, it does demonstrate that an exponential decay for f^{RS} is predicted. An approximate correction to the bound given by (4.5.13) may be obtained by substituting (4.6.17) back into (4.6.13) and neglecting the double integral. We get

$$(a^2/3\eta) \langle K^* \rangle \left\{ 1 + \int \frac{(\rho_{B|R} - \rho_B)}{|x_B - x_R|} dx_B - a^2 \int \frac{\exp(-\beta |x_B - x_R|)}{|x_B - x_R|^2} \rho_{B|R} \, dx_B + \tfrac{1}{5}\eta(5 - \eta) \right\} = \bar{c}, \tag{4.6.19}$$

although the estimate supplied by (4.6.19) is no longer necessarily a bound.

4.7 Perturbation Theory

In the limit $\eta \ll 1$, it is possible to obtain a solution of the integral equation (4.3.7), together with (4.3.8), in the form of a perturbation series. The problem has not been studied previously in this formulation but the outline to follow is closely related to work of Brailsford (1976) on the diffusion problem and work of Hinch (1977) on problems for viscous fluids. In each case, the methods of solution are variants of one proposed by Lax (1952) in the context of scattering problems.

We start by writing equation (4.3.7) explicitly in the form

$$\int_{\partial V_A} \zeta(x,x')\, q^A(x)\, dS + \Big\{ \sum_{B \neq A}{}' \Big[\int_{\partial V_B} \zeta(x,x')\, q^B(x)\, dS + K^* \int_{V_B} \zeta(x,x')\, dx \Big] - K^* \int_{V \setminus V_A} \zeta(x,x')\, dx \Big\} + \bar{c} = 0, \quad x' \in \partial V_A, \; A = 1,2,\ldots N, \tag{4.7.1}$$

in which q^A denotes the restriction of q to ∂V_A. K* satisfies (4.3.21) but, assuming statistical uniformity, K* is identified with its expectation value $\langle K^* \rangle$. Taking the expectation of equation (4.7.1), conditional on the void A being fixed, now gives

$$\int_{\partial V_A} \zeta(x,x')\, q^A_A(x)\, dS + \int_{V \setminus V_A} \Big\{ \Big[\int_{\partial V_B} \zeta(x,x')\, q^B_{AB}(x)\, dS + \langle K^* \rangle \int_{V_B} \zeta(x,x')\, dx \Big] \rho_{B|A} - \langle K^* \rangle \zeta(x_B,x') \Big\} dx_B + \bar{c} = 0, \quad x' \in \partial V_A \tag{4.7.2}$$

in which $q^A_A(x)$ denotes the expected value of $q^A(x)$, conditional upon x_A being fixed, and $q^B_{AB}(x)$ the expected value of q^B conditional upon x_A and x_B being fixed. Now at low concentrations of voids, few voids will be close together and it is reasonable to postulate that

$$q^B_{AB}(x) \sim q^B_B(x) \tag{4.7.3}$$

with an error that is serious only for the few voids that are close.

This approximation is identical in form to the 'quasicrystalline approximation' of Lax (1952). If we adopt it as an identity, equation (4.7.2) becomes an integral equation for $q_A^A(x)$ which yields, in fact, precisely the equation (4.5.13) for $\langle K^* \rangle$. Thus although the above reasoning strictly justifies retention only of the lowest order terms in (4.5.13), it is interesting to note that (4.7.3), if taken literally, in fact yields a lower bound for $\langle K^* \rangle$. A similar observation for the 'overall modulus' problem was made by Willis (1979).

A better approximation may be obtained, essentially following Hinch (1977) and Brailsford (1976), by generating an equation for $q_{AB}^A(x)$ from the expectation of (4.7.1) conditional upon x_A and x_B being fixed. This produces an equation like (4.7.2), except that it involves $q_{ABC}^C(x)$ as well. An appropriate closure assumption, analogous to (4.7.3), is that

$$q^c_{ABc}(x) \sim q^c_{Ac}(x) + q^c_{Bc}(x) - q^c_c(x); \qquad (4.7.5)$$

this is seriously in error only when all three voids are close. Following through the details, retaining only the two terms of lowest order, this time yields a result that is consistent with (4.6.19).

Under the assumptions of §5, it emerged that q^A was constant except close to ∂V, so that $q^A \approx q_A^A$. Also, because q^A was independent of the position of other voids, the quasicrystalline approximation was realized exactly. In §6, however, it emerged that r^A was constant and f^{AB} was translation-invariant. If we accept these conclusions, then

$$q^c_{ABc} = q^c_{Ac} + q^c_{Bc} - q^c_c + \int f^{cD}\left[\rho_{D|ABc} - \rho_{D|Ac} - \rho_{D|Bc} + \rho_{D|c}\right] dx_D \qquad (4.7.6)$$

in which the integrand is only significant when the voids A, B and C are close, since the medium has no long range order. It is therefore, not a total surprise that (4.7.3) generates (4.5.13) exactly while (4.7.5) is consistent with a two term expansion of (4.6.19). We note however, that perturbation theory of this

type makes heavy demands upon physical intuition in disregarding boundary layer terms that a more careful analysis shows are in some initial danger of dominating the solution, coming, as they do, from integrals that could become unbounded as V becomes indefinitely large.

4.8 Results and Discussion

The main results of this chapter are the bound $\langle K^* \rangle$ for $\langle K' \rangle$ contained in equation (4.5.13) and the low concentration approximation given by (4.6.19). It is convenient to express the results in terms of the mean normalized flux F into each void:

$$F = n^{-1}\langle K' \rangle (1-\eta)/\bar{c} = (4\pi a^3/3\eta\bar{c})(1-\eta)\langle K' \rangle. \tag{4.8.1}$$

We also simplify equations (4.5.13) and (4.6.19) by setting

$$\rho_A = \eta, \tag{4.8.2}$$

and

$$\rho_{B|A} = n\, g(x), \tag{4.8.3}$$

where

$$x = |x_B - x_A|/2a. \tag{4.8.4}$$

Performing the trivial angular integration now gives, from (4.5.13), the lower bound

$$F_1 = 4\pi a (1-\eta)\left[1 - 5\eta - \tfrac{1}{5}\eta^2 + 12\eta \int_1^\infty (g(x)-1)\, x\, dx\right]^{-1}, \tag{4.8.5}$$

and, from (4.6.19), the estimate

$$F_2 = 4\pi a(1-\eta)\left[1 - 5\eta - \tfrac{1}{5}\eta^2 + 2\eta \int_1^\infty (g(x)-1)\, x\, dx - 6\eta \int_1^\infty \exp\left(-2(3\eta)^{1/2}x\right) g(x)\, dx\right]^{-1}. \tag{4.8.6}$$

The latter is only valid at small values of η and so could equally well be expanded in powers of η.

Before we proceed, it may be remarked that the restriction to a fixed number N of voids may be relaxed, by regarding the expectations so far derived as being conditional upon N and then taking expectations over N, the mean number density n now being interpreted as $\langle N \rangle / V$.

The pair distribution function g(x) is zero for $0 \leq x < 1$ since the voids are not allowed to overlap, and tends to 1 as $x \to \infty$ It must, in fact, also satisfy some other restrictions if it is to arise from any stochastic mixing process. Although a complete set of restrictions is unknown, we can illustrate this remark by considering the 'well-stirred' approximation defined by

$$g(x) = 1 \quad , \quad 1 < x < \infty \, , \qquad (4.8.7)$$

which has been used in the low-concentration limit by Batchelor and Green (1972) and Willis and Acton (1976), for example, and at arbitrary concentrations by Varadan et al. (1978) in different physical contexts. When (4.8.7) is substituted into (4.8.5), the integral disappears and we see that the lower bound F_1 becomes infinite at a value of just less than 0.2. Since we obtained F_1 from the expectation value of a functional that plainly remains finite, we conclude that the well-stirred approximation (4.8.7) is untenable at concentrations around or above 0.2. At very high concentrations, it is plausible that g(x) should rise above 1 when x is close to 1, since knowledge that a sphere is centred at a given point must almost guarantee the presence of spheres close to x=1 when the spheres are rather tightly packed. The integral in the denominator of (4.8.5) is then likely to be positive and should ensure that F_1 remains finite.

In view of the sensitivity of F_1 and F_2 to the form of g(x), we abandon the study of abstractions such as (4.8.7) and instead substitute some genuinely plausible forms for g(x). The first two are rigorously attainable, having been derived by Matérn (1960) from explicitly defined stochastic models. The simpler of Matérn's models is obtained by sampling a Poisson process of intensity α and deleting any point which is within 2a of any other, whether or not this has already been deleted.

For this model,

$$\eta = v\alpha\, e^{-8v\alpha}, \tag{4.8.8}$$

where $v = \frac{4}{3}\pi a^3$, and

$$g(x) = \exp\left[v\alpha\,(16 - \phi(x))\right], \quad 1 \leq x < \infty, \tag{4.8.9}$$

where

$$\left.\begin{aligned} \phi(x) &= 8 + 6x - \tfrac{1}{2}x^3, && 0 \leq x \leq 2, \\ &= 16, && 2 \leq x < \infty, \end{aligned}\right\} \tag{4.8.10}$$

so that $v\,\phi(x)$ represents the volume of the region occupied by two spheres, each of radius 2a, whose centres are 2ax apart. It may be noted that $g(x) = 1$ for $x \geq 2$, while $g(x) > 1$ for $1 \leq x < 2$, taking its maximum value $\exp(\frac{27}{2}\, v\alpha)$ at $x = 1$. Thus, the model displays some 'piling up' of probability around $x = 1$, even at low concentrations. The model is limited, however, in allowing only low concentrations, the maximum value of η being approximately 0.046, attained when $v\alpha = 1/8$.

In Matern's second model, the points of a Poisson process of intensity α are independently marked with a uniformly distributed birth time on (0,1) so that they are, in effect, generated from a Poisson process on $R^3 \times (0, 1)$. Any given point is retained if no point within 2a has an earlier birth time. With the slightly unnatural inclusion of points already deleted in applying this criterion, Matern was able to show that

$$\eta = \frac{1}{8}\left(1 - e^{-8v\alpha}\right), \tag{4.8.11}$$

and

$$g(x) = \frac{16\,\phi(x)(1 - e^{-8v\alpha}) - 128\,(1 - e^{-v\alpha\,\phi(x)})}{\phi(x)(\phi(x) - 8)(1 - e^{-8v\alpha})^2}, \quad 1 \leq x < \infty. \tag{4.8.12}$$

Again, $g(x)=1$ when $x \geqslant 2$ and is greatest when $x = 1$. The range of concentrations is not as limited as in Matern's first model, but still $\eta \lesssim 1/8$. The functions $g(x)$ corresponding to each of these models are graphed in figure 4.1, for $\eta = 0.046$, the limit of validity of the first. Plots of the bounds F_1, and of the estimates F_2, are displayed in figure 4.2. At low concentrations ($v\alpha \to 0$), both of Matern's models reduce to the well-stirred approximation (4.8.7) and F_1 and F_2 associated with this approximation are also shown. Each model gives as $\eta \to 0$,

$$F_2 \sim 4\pi a \left(1+(3\eta)^{1/2}\right), \qquad (4.8.13)$$

which is precisely consistent, to this order, with the self-consistent approximation generated from (4.2.13).

In the absence of any precisely realizable $g(x)$ valid at arbitrary concentrations, plots of F_1 and F_2 associated with the Percus-Yevick hard-sphere approximation are given in figure 4.3. Percus and Yevick (1957) generated an integral equation that $g(x)$ should approximately satisfy by treating a statistical mechanical system of hard spheres, with one sphere in a fixed position, as a perturbation of the system with that particular sphere absent. The Percus-Yevick equation was solved by Wertheim (1963) who found the Laplace transform of $xg(x)$ in closed form, and $g(x)$ has been tabulated by Throop and Bearman (1964). A typical plot of $g(x)$, taken from this tabulation, with $\eta = \pi/10$ so that $8na^3 = 0.6$, is shown in figure 4.4. It is a fortunate coincidence that the integral in the bound (4.8.5) contains the integral of $xg(x)$ and so can be obtained analytically from the small argument asymptotic behaviour of the Laplace transform. The result, obtained with the aid of Wertheim's expression is

$$\int_1^\infty (g(x)-1)x\,dx = \frac{1}{2} - \frac{10-2\eta+\eta^2}{20(1+2\eta)}. \qquad (4.8.14)$$

We note that this isequivalent to the expression given in Talbot and Willis (1980). For values of η up to about 0.3, the result (4.8.14) agrees well with a numerical evaluation obtained from the tabulation of Throop and Bearman (1964), but thereafter the oscillating tail that remains for $x > 4$, the limit of the tabulation, is significant.

The estimate F_2, obtained from equation (4.8.6), contains a further integral that has to be evaluated numerically. The plot of F_2 against η displays a singularity for η around 0.27, showing that the perturbation has broken down by this stage. However, at lower values of η, say up to 0.1, which is probably around the limit of validity of the approximation, the effect of replacing g(x) by 1 is in fact small, so that a fair analytic approximation to F_2 can be generated throughout its range of usefulness.

Also shown in figure 4.3 is a plot of F as calculated from the self consistent equation (4.2.13). It follows the approximation F_2 at low concentrations but actually lies below the lower bound F_1 when η is greater than 0.2, approximately. Exactly what distribution it approximates, if any, at higher concentrations, is uncertain.

Finally, we construct a distribution of 'well-separated' type in which the spheres centres are separated by at least $2kn^{-1/3}$. A distribution with this property could be realized in statistical mechanics by making the interaction energy between a pair of spheres infinite if their centres are separated by less than 2kn. Thus, they behave like spheres of radius $a' = kn^{-1/3}$ and a pileup of probability is to be expected around their minimum separation. If x is now defined as $|x_B - x_A| / 2a'$ it follows that $P_{B|A}$ is given by (4.8.3), where g(x) is the pair distribution function corresponding to spheres of radius a' at number density n. F_1 and F_2 then take the forms

$$F_1 = 4\pi a(1-\eta)\left[1+\eta-\tfrac{1}{5}\eta^2-6\eta^{1/3}\left(\tfrac{4}{3}\pi\right)^{2/3}\kappa^2+12\left(\tfrac{4}{3}\pi\right)^{2/3}\kappa^2\eta^{1/3}\int_1^\infty (g(x)-1)\,x\,dx\right]^{-1},$$

(4.8.15)

$$F_2 = 4\pi a(1-\eta)\left[1+\eta-\tfrac{1}{5}\eta^2-6\eta^{1/3}\left(\tfrac{4}{3}\pi\right)^{2/3}\kappa^2+12\left(\tfrac{4}{3}\pi\right)^{2/3}\kappa^2\eta^{1/3}\int_1^\infty (g(x)-1)\,x\,dx\right.$$

$$\left.-6\eta^{2/3}\left(\tfrac{4}{3}\pi\right)^{1/3}\kappa\int_1^\infty \exp\left[-2\sqrt{3}\left(\tfrac{4}{3}\pi\right)^{1/3}\kappa\eta^{1/6}x\right](g(x)-1)\,dx\right]^{-1}.$$

(4.8.16)

The possible validity of this approximation is limited by the requirement that $a' \geq a$, from which it follows that

$$\eta \leq \frac{4}{3}\pi\kappa^3. \qquad (4.8.17)$$

The concentration $\eta' = 4\pi n a'^3/3$ from which g(x) is calculated remains constant at $\frac{4}{3}\pi k^3$, and, for realizability, this must be less than the density for maximum packing. This is given by Hansen and McDonald (1976) as $\pi/3\sqrt{2}$ and a concentration around 0.5 is considered to be close to crystallization.

It is interesting to note that, as $\eta \to 0$, (4.8.15) gives

$$F_1 \sim 4\pi a\left[1 + 6\left(\tfrac{4}{3}\pi\right)^{2/3}\kappa^2\eta^{1/3}\left(1 - 2\int_1^\infty (g(x)-1)\,x\,dx\right)\right]. \qquad (4.8.18)$$

This lies above both the bound F_1 and the estimate F_2 obtained from the well-stirred approximation, which all of our earlier models approach in this limit. Plots of the bound (4.8.15) and the estimate (4.8.16) are shown in figure 4.5, for g(x) as in the Percus-Yevick approximation, with k chosen as 0.4217. This corresponds to $8na^{1/3} = 0.6$, or $\eta' = \pi/10$, for which g(x) is shown in figure 4.3. The values of F_1 and F_2 coincide with those obtained from the 'ordinary' Percus-Yevick approximation when $\eta = \eta'$, as they should, and are greater than the corresponding 'ordinary' values for $\eta < \eta'$.

In conclusion, we note the sensitivity of the sink strength to the precise distribution of the voids. In practice, pair distribution functions will be unknown and then the simple self-consistent estimate seems a natural choice: it is adequate at low void densities and could be modified to allow for a well separated distribution by placing a sink-free region adjacent to the void to be considered explicitly analogously to the pseudo-effective medium approach of Brailsford and Bullough (1976) to arrays of dislocations considered in chapter 2. At higher void densities, however, the self-consistent estimate may be in error and use of the bound (4.8.5) would seem to be preferable, even with the pair distribution function estimated in some approximate way.

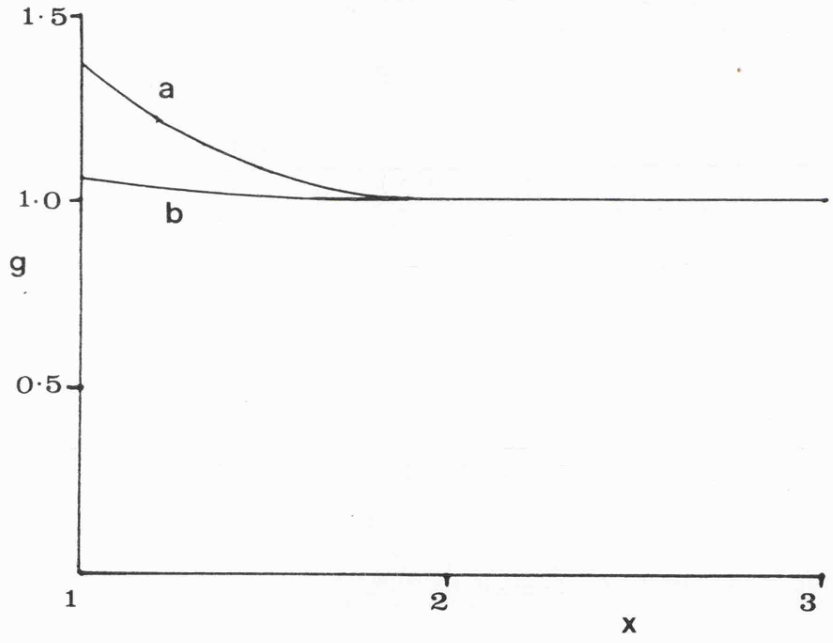


Figure 4.1 Plots of the pair distribution function g(x), at volume density η = 0.046, for the two Matern models: (a) given by equation (4.8.7) and (b) given by equation (4.8.10).

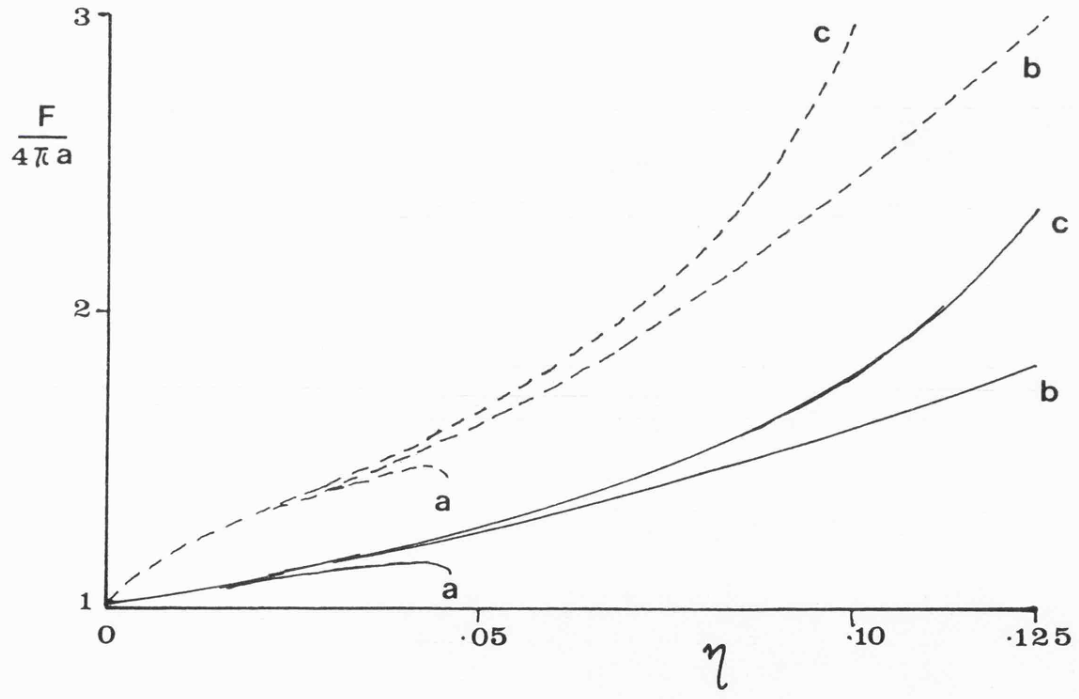


Figure 4.2 Plots of lower bound estimates F_1 (continuous lines) and low-concentration approximations F_2 (dashed lines) for the two Matern models (a) and (b) and for the well-stirred approximation (c).

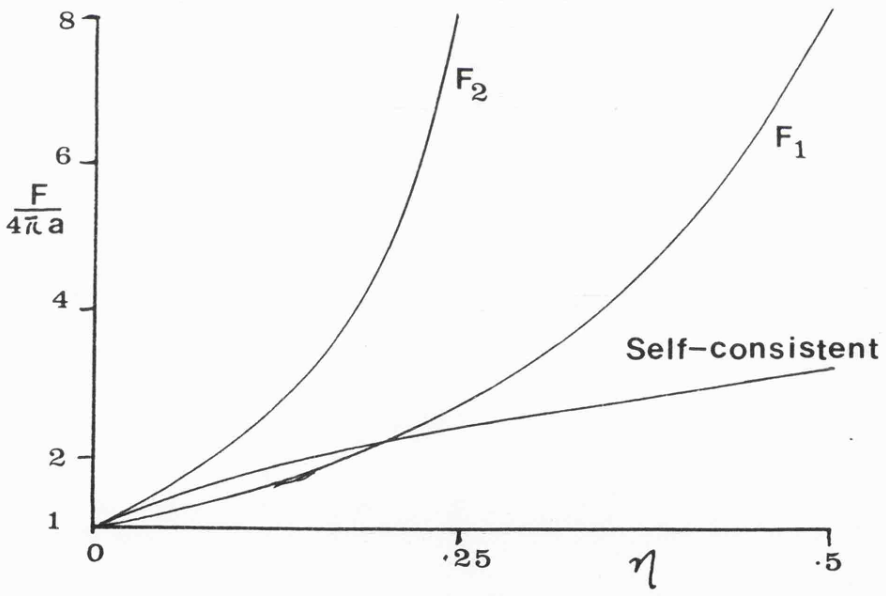


Figure 4.3 Plots of lower bound estimate F_1 and low-concentration approximation F_2 for the Percus-Yevick model. The self-consistent approximation is also shown.

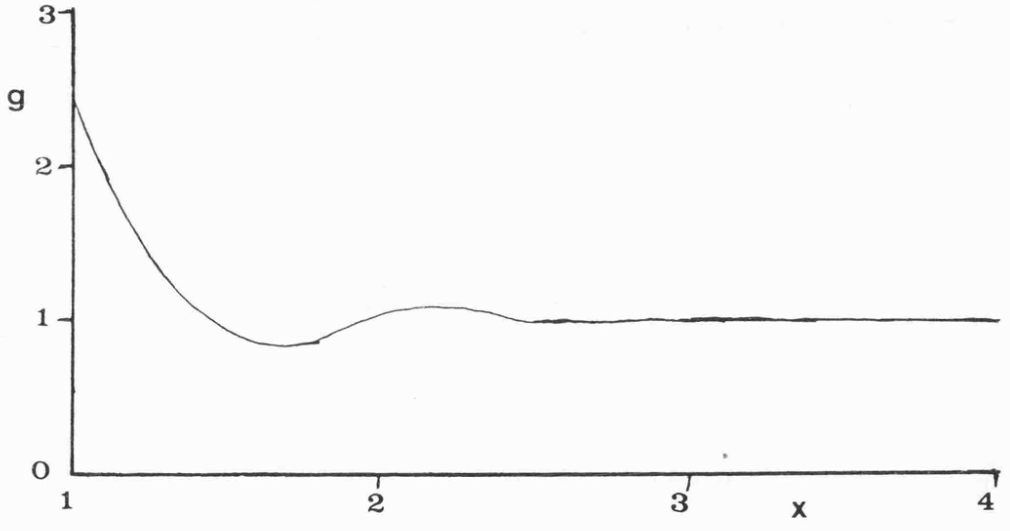


Figure 4.4 The Percus-Yevick pair distribution function g(x) at volume density $\eta = \pi/10$.

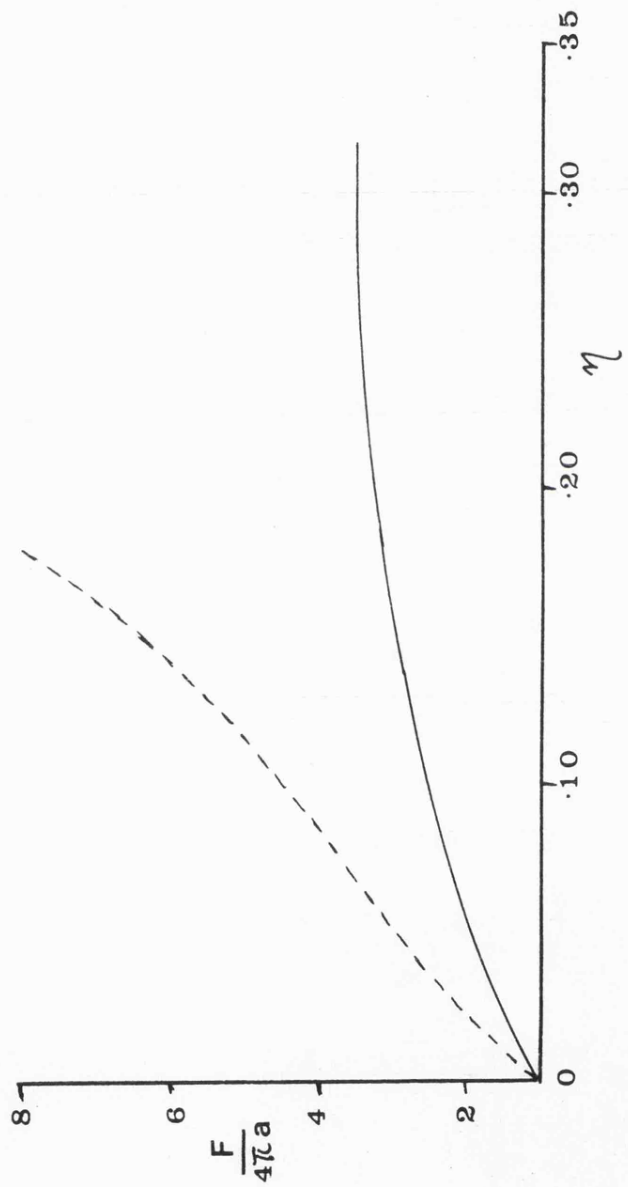


Figure 4.5 The lower bound (continuous line) and low-concentration approximation (dashed line) for the well-separated model.

5. Improved Self Consistent Estimates

5.1 Introduction

In this final chapter we turn our attention to obtaining self consistent estimates for the overall sink strength of an array of voids which take some account of correlations between the sinks. In the process we generate a procedure which avoids the convergence problems encountered in chapter 4.

The basis of the approach is to consider the actual medium we wish to study as a limiting case of a lossy material whose sink strength per unit volume is a random function of position. In analogy with the momentum polarization defined by Willis (1980) we introduce a concentration polarization using a homogeneous lossy comparison medium. The resulting differential equation is then reformulated as an integral equation, using the Green function for the lossy comparison material, which could be solved by perturbation theory of the type described in 4.7. Our approach here is to present a variational formulation of the integral equation and demonstrate its relation to a classical variational principle. The development is closely related to work of Willis (1981a) on the elastodynamics of heterogeneous materials.

Finally, we substitute simple trial fields in the variational principle and obtain self consistent estimates for the overall sink strength of the medium by choosing the comparison medium to have the properties of the overall material.

5.2 Formulation in Terms of Polarizations

As in chapter 4 we again consider a body occupying a region V (with boundary ∂V) containing exactly N identical spherical sinks centred at x_A, A=1, ..., N, each of radius a . The region occupied by the sinks will be denoted V_v with boundary ∂V_v. In contrast to the problem considered in chapter 4 we do not assume ab initio that the sinks are perfect, so that the boundary condition (4.2.3) on ∂V_v does not apply. Instead we assume that both sinks and matrix are composed of 'lossy' materials having sink strengths β_1^2 and β_2^2 respectively, and study the equations

$$D_1 (\nabla^2 c - \beta_1^2 c) + K(x) = 0 , \quad x \in V_V , \tag{5.2.1}$$

$$D_2 (\nabla^2 c - \beta_2^2 c) + K(x) = 0 , \quad x \in V \setminus V_V \tag{5.2.2}$$

together with the boundary condition

$$\partial c / \partial n = 0 , \quad x \in \partial V , \tag{5.2.3}$$

and suitable continuity conditions on ∂V_V. In (5.2.1), (5.2.2) D_1, D_2 are the diffusion coefficients for V_V and $V \setminus V_V$ and K(x) is the generation rate of defects. The explicit dependence on the diffusion coefficients is removed by combining (5.2.1), (5.2.2) to get the single equation

$$\nabla^2 c - \beta^2 c + K'(x) = 0 , \quad x \in V , \tag{5.2.4}$$

which is to be interpreted in the sense of distributions. The function β^2 in (5.2.4) is defined by

$$\begin{aligned} \beta^2 &= \beta_1^2 , \quad x \in V_V \\ &= \beta_2^2 , \quad x \in V \setminus V_V \end{aligned} \tag{5.2.5}$$

We see that, in the limit $\beta_1 \to \infty$, $\beta_2 \to 0$ with K' non-zero and constant only over $V \setminus V_V$, (5.2.4) together with (5.2.3) reduces to the system studied in chapter 4.

The overall sink strength, k^2, of the body is defined in terms of the volume averages of c and K', $\bar{c}$ and $\bar{K}'$, by

$$\bar{c} = \bar{K}' / \kappa^2 , \tag{5.2.6}$$

where

$$\bar{c} = \frac{1}{V} \int_V c(x) \, dx , \tag{5.2.7}$$

$$\bar{K}' = \frac{1}{V} \int_V K'(x) \, dx . \tag{5.2.8}$$

We now introduce a homogeneous comparison body having constant sink strength β_0^2 and define a polarization concentration $\bar{\pi}$ by

$$\bar{\pi} = (\beta^2 - \beta_0^2)c; \tag{5.2.9}$$

then in terms of $\bar{\pi}$, (5.2.4) can be written

$$\nabla^2 c - \beta_0^2 c - \bar{\pi} + K' = 0. \tag{5.2.10}$$

The polarization $\bar{\pi}$ is in direct correspondence to the momentum polarization introduced by Willis (1980). We define a Green function for the reference body by the equation

$$\nabla^2 \varsigma(x,x') - \beta_0^2 \varsigma(x,x') = \delta(x-x'), \quad x \in V, \tag{5.2.11}$$

$$\frac{\partial \varsigma}{\partial n} = 0, \quad x \in \partial V, \tag{5.2.12}$$

and note that it is easy to show that G is symmetric in its arguments. The usual argument using Gauss's theorem gives the representation

$$c(x') = \int_V \varsigma(x,x') \left[\bar{\pi}(x) - K'(x)\right] dx, \tag{5.2.13}$$

for the concentration c. In the same way as in Willis (1980), substituting (5.2.13) into (5.2.9) yields the integral equation

$$(\beta^2 - \beta_0^2)^{-1} \bar{\pi} - \int_V \varsigma(x,x') \left[\bar{\pi}(x) - K'(x)\right] dx = 0, \quad x' \in V, \tag{5.2.14}$$

for $\bar{\pi}$. Furthermore, integrating (5.2.10) yields the consistency condition

$$\bar{K}' = \beta_0^2 \bar{c} + \bar{\pi}, \tag{5.2.15}$$

so that with K' prescribed, the solution of (5.2.14) yields $\bar{c}$ through (5.2.15) and hence the overall sink strength through (5.2.6).

Finally we write (5.2.14) in the compact form

$$(\beta^2-\beta_0^2)^{-1}\bar{\pi} - \bar{\Gamma}\bar{\pi} + \bar{\Gamma}K' = 0, \quad x' \in V, \tag{5.2.16}$$

where $\bar{\Gamma}$ is the Green function operator.

5.3 Variational Principles

We noted earlier that the Green function is symmetric so that the integral equation (5.2.16) is equivalent to the variational statement

$$\delta \mathcal{H}(\bar{\pi}) = 0 \tag{5.3.1}$$

where

$$\mathcal{H}(\bar{\pi}) = \int_V dx \left\{ \bar{\pi}(\beta^2-\beta_0^2)^{-1}\bar{\pi} - \bar{\pi}\bar{\Gamma}\bar{\pi} + 2\bar{\pi}\bar{\Gamma}K' \right\}. \tag{5.3.2}$$

The operator $\bar{\Gamma}$ can be shown to be negative semi-definite so that (5.3.1) will only be an extremum principle when $(\beta^2-\beta_0^2)^{-1}$ is a positive operator.

Although we could use (5.3.1) immediately, it is not the strongest statement that can be made. We will show that a classical formulation of the differential equation (5.2.4) as a variational principle yields (5.3.1) if certain quadratic terms are neglected. This is analogous to the elastostatic problem where the variational principle of Hashin and Shtrikman (1962) is obtained from the classical energy principles in the same way. This was demonstrated by Hill (1963) and by Willis (1981b). The present problem is more closely related to the elastodynamic problem because of the direct correspondence between $\bar{\pi}$ and the momentum polarization. Variational principles for the elastodynamics of inhomogeneous media have been given by Willis (1981a) and the subsequent development closely resembles their derivation.

For all sufficiently smooth c and w equation (5.2.4) implies that

$$\int_{\partial V} ds \left\{ w \frac{\partial c}{\partial n} \right\} - \int_V dx \left\{ \nabla c . \nabla w + \beta^2 c w - K' w \right\} = 0, \qquad (5.3.3)$$

so that use of the boundary condition (5.2.3) gives

$$\int_V dx \left\{ \nabla c . \nabla w + \beta^2 c w - K' w \right\} = 0. \qquad (5.3.4)$$

Conversely, for all suitable w, (5.3.4) implies (5.2.4) and the boundary condition (5.2.3). Thus (5.3.4) is a weak formulation of the problem. Now consider

$$\mathcal{J}(c) = \int_V dx \left\{ (\nabla c)^2 + \beta^2 c^2 - 2K'c \right\}, \qquad (5.3.5)$$

then the statement

$$\delta \mathcal{J}(c) = 0, \qquad (5.3.6)$$

generates (5.3.4) with $w = \delta c$ so that c is characterized as a weak solution of the problem.

For any $\bar{\pi}$ the representation (5.2.13) generates suitable trial fields for substitution into (5.3.5). Also, c given by (5.2.13) satisfies the differential equation (5.2.10) so that

$$\int_V dx \left\{ (\nabla c)^2 + \beta_0^2 c^2 + \bar{\pi} c - K' c \right\} = 0. \qquad (5.3.7)$$

We set

$$\delta\beta^2 = \beta^2 - \beta_0^2, \qquad (5.3.8)$$

and use (5.3.7) to write (5.3.5) as

$$\mathcal{J}(c) = \int_V dx \left\{ \delta\beta^2 c^2 - K' c - \bar{\pi} c \right\}. \qquad (5.3.9)$$

The first term in (5.3.9) can now be expanded to get

$$\delta\beta^2 c^2 = (\delta\beta^2 c - \bar{\pi})(\delta\beta^2)^{-1}(\delta\beta^2 c - \bar{\pi}) + 2\bar{\pi}c - (\delta\beta^2)^{-1}, \tag{5.3.10}$$

and substituting this into (5.3.9) gives

$$\mathcal{J}(c) = \mathcal{H}_1(c) + \int_V dx\,(\delta\beta^2 c - \bar{\pi})(\delta\beta^2)^{-1}(\delta\beta^2 - \bar{\pi}), \tag{5.3.11}$$

where

$$\mathcal{H}_1(c) = \int_V dx\,\left\{(\bar{\pi} - K')c - (\beta^2 - \beta_0^2)^{-1}\bar{\pi}^2\right\}. \tag{5.3.12}$$

The second term on the right hand side of (5.3.11) is quadratic in $\delta\beta^2 c - \bar{\pi}$ and so the principle (5.3.6) implies

$$\delta\mathcal{H}_1(c) = 0 \tag{5.3.13}$$

Finally, if we use the representation (5.2.13), $\mathcal{H}_1$ can be written

$$\mathcal{H}_1 = -\mathcal{H}(\bar{\pi}) + \int_V dx\,K'\Gamma K', \tag{5.3.14}$$

and hence, because K' is prescribed, (5.3.13)in turn implies

$$\delta\mathcal{H}(\bar{\pi}) = 0 \tag{5.3.15}$$

where $\mathcal{H}$ is given by (5.3.2).

When $\delta\beta^2$ is negative (5.3.11) provides an upper bound for the true $\mathcal{J}(c)$. We thus see that in this case the statement (5.3.1) is weaker than the classical statement (5.3.6) as it was derived by neglecting a negative quadratic term on the right side of (5.3.11). We will make no further use of the classical principle.

5.4 Application to Random Distributions of Sinks

We now use the variational principle (5.3.1) to obtain estimates for the overall sink strength of random distributions of sinks. We will consider the limit

$$\beta_1 \to \infty \tag{5.4.1}$$

$$\beta_2 \to 0 \tag{5.4.2}$$

so that the sinks are perfect, and will assume that the generation rate K' is only non-zero on $V \setminus V_v$ where it is constant.

As before, the configuration of the body will be regarded as labelled with a parameter α taken from a sample space $\mathcal{S}$ over which a probability density $p(\alpha)$ is defined. In principle, the integral equation (5.2.14) could be solved for any given α yielding $\pi(x, \alpha)$ and hence a value of $\bar{c}$ dependent on α. It would seem plausible, that, for a large statistically uniform body, $\bar{c}$ should become independent of the configuration and coincide with its expectation value defined by

$$\langle \bar{c} \rangle = \int_{\mathcal{S}} \bar{c}(\alpha)\, p(\alpha)\, d\alpha , \tag{5.4.3}$$

A reasonable procedure, then, is to replace the consistency condition (5.2.15) by

$$\langle \bar{K}' \rangle = \langle \bar{\pi} \rangle + \beta_0^2 \langle \bar{c} \rangle , \tag{5.4.4}$$

the defining relation for the overall sink strength by

$$\langle \bar{K}' \rangle = K^2 \langle \bar{c} \rangle , \tag{5.4.5}$$

and to estimate $\langle \bar{\pi} \rangle$ by seeking a stationary point of $\langle \mathcal{H} \rangle$ within some subspace of functions whose domain is $V \times \mathcal{S}$.

Recently, Papanicolau (1980) has analysed a class of problems which include

$$\nabla^2 c - u^2 c + K' = 0 , \quad x \in V, \tag{5.4.6}$$

$$c = 0 , \quad x \in \partial V, \tag{5.4.7}$$

where u^2 is a bounded random function of position; then if h is a correlation length relating to u^2, he showed that in the limit $uh \to 0$ (6.4.6) can be replaced by

$$\nabla^2 \langle c \rangle - \langle u^2 \rangle \langle c \rangle + \langle K' \rangle = 0 , \tag{5.4.8}$$

so that the overall sink strength k^2 is given by

$$k^2 = \langle u^2 \rangle \tag{5.4.9}$$

It is easy to show that in this limit, use of the procedure outlined above reproduces (6.4.9) exactly. Thus there is some justification for adopting it in the present context, even though the limit $u \to \infty$ will be taken in the sinks.

Proceeding to details, we denote the region occupied by the sink centred at x_A by V_A and its boundary by ∂V_A. From its definition $\bar{\pi}$ can be written

$$\bar{\pi} = (\beta^2 - \beta_2^2) c + (\beta_2^2 - \beta_0^2) c , \tag{5.4.10}$$

where the first term is only non-zero for $x \in V_A$, $A=1,\ldots,N$ and the second is defined throughout V. We are thus led to consider a trial function given by

$$\pi = \sum_{A=1}^{N}{}' \bar{\pi}^A + \bar{\pi}_2 , \tag{5.4.11}$$

where $\bar{\pi}^A$ is only defined on V_A and $\bar{\pi}_2$ is constant throughout V.

The form of π^A we take is given by

$$\bar{\pi}^A = \bar{\pi}_A f_A(x), \tag{5.4.12}$$

where

$$f_A(x) = \frac{a\beta_1 \sinh(\beta_1|x-x_A|)}{|x-x_A| \cosh(\beta_1 a)}, \tag{5.4.13}$$

and $\bar{\pi}_A$ is constant (possibly depending on x_A) and non-zero only in V_A. The choice of (5.4.13) follows from the solution of the problem of one sink embedded in matrix material when $\beta_1 >> 1$. Also, in the limit $\beta_1 \to \infty$, the functions f_A behave as distributions of sinks on the surfaces ∂V_A.

The choice of $\bar{\pi}_2$ constant throughout V is perhaps not a good one, as in the neighbourhood of a sink the concentration might be expected to change rapidly. However it is the simplest assumption that can be made. A different approach to the integral equation (5.2.14) is to take conditional expectations of the equation to obtain an infinite hierarchy of equations involving conditional averages of $\bar{\pi}$. The hierarchy is then closed by making some assumption, such as the quasicrystalline approximation of Lax (1952), which is strictly valid only in the limit of low concentrations. In fact, the choice of $\bar{\pi}_2$ constant is consistent with the type of closure assumption made, for example, by Devaney (1980) in the context of scattering of elastic waves.

We now substitute (5.4.11) into (5.3.2) to obtain

$$\mathcal{H}(\bar{\pi}) = \int_V dx \Big\{ \Big(\sum_A{}' \bar{\pi}_A f_A + \bar{\pi}_2 \Big)(\beta^2 - \beta_0^2)^{-1} \Big(\sum_B{}' \bar{\pi}_B f_B + \bar{\pi}_2 \Big)$$

$$+ \frac{2\bar{\pi}_2}{\beta_0^2 V} \int dx' \sum_A{}' f_A \bar{\pi}_A + \frac{\bar{\pi}_2^2}{\beta_0^2} + 2\Big[\sum_A{}' f_A \bar{\pi}_A + \bar{\pi}_2 \Big] \int dx' \zeta(x,x') K' \Big\}$$

$$- \int dx \sum_A{}' \Big[\bar{\pi}_A f_A \int dx' \zeta(x,x') \bar{\pi}_A f_A + \bar{\pi}_A f_A \sum_{B \neq A}{}' \int dx' \zeta(x,x') \bar{\pi}_B f_B \Big], \tag{5.4.14}$$

where we have used the mean value and symmetry of G to simplify some of the integrals. Equation (5.4.14) can be reduced further in the limit $\beta_1 \to \infty$, $\beta_2 \to 0$: the only term causing any difficulty being that involving K', which is only non-zero over $V \setminus V_v$. Explicitly,

$$\int_V dx \left[\sum_A' f_A \bar{\pi}_A + \bar{\pi}_2 \right] \int dx' \varrho(x,x') K'$$

$$\to \left\{ \sum_A' \int_{\partial V_A} dx\, \bar{\pi}_A + \int_V dx\, \bar{\pi}_2 \right\} \int_{V \setminus V_v} dx' \varrho(x,x') K', \tag{5.4.15}$$

as $\beta_1 \to \infty$. The right hand side can be expanded and the mean value of G used to get

$$-(V-V_v)\frac{\bar{\pi}_2 K'}{\beta_0^2} - \frac{K'}{\beta_0^2} \sum_A' \int_{\partial V_A} dx\, \bar{\pi}_A - K' \sum_A' \int_{\partial V_A} dx\, \bar{\pi}_A \sum_B' \int_{V_B} dx' \varrho(x,x'). \tag{5.4.16}$$

Using (5.4.16) we find that, in the limit, $\mathcal{H}(\bar{\pi})$ becomes

$$\mathcal{H}(\bar{\pi}) = \int_V dx \left\{ \eta \frac{\bar{\pi}_2^2}{\beta_0^2} + \frac{2\bar{\pi}_2}{V\beta_0^2} S_0 \sum_A' \bar{\pi}_A - 2(1-\eta) \frac{\bar{\pi}_2}{\beta_0^2} K' \right\}$$

$$- \sum_A' \bar{\pi}_A \left\{ \bar{\pi}_A T_{AA} + 2K' S_{AA} + \sum_{B \neq A} (\bar{\pi}_B T_{AB} + 2K' S_{AB}) + \frac{2K'}{\beta_0^2} S_0 \right\}, \tag{5.4.17}$$

where $S_0 = 4\pi a^2$ is the surface area of a sink, η is the volume concentration of sinks and T_{AB}, S_{AB} are defined below:

$$T_{AB} = \int_{\partial V_A} dx \int_{\partial V_B} dx' \varrho(x,x'), \tag{5.4.18}$$

$$S_{AB} = \int_{\partial V_A} dx \int_{V_B} dx' \varrho(x,x'). \tag{5.4.19}$$

We now need the functions T_{AB}, S_{AB}. First the Green function G can be expressed in terms of the infinite body Green function G as

$$\zeta(x,x') = \zeta^{\infty}(x,x') + \int_{\partial V} \zeta(x,x'') \zeta^{\infty}(x',x'')\, dx'', \tag{5.4.20}$$

where the integral term is symmetric in x, x'. Thus the integrals in (5.4.18), (5.4.19) can be evaluated using results for G^{∞}. Using standard addition theorems and denoting the integral in (5.4.20) by G*, we obtain the following results:

$$\begin{aligned} T_{AA} &= -a S_0 C + S_0^2 A^2 \zeta^*_{AA} \\ T_{AB} &= S_0^2 A^2 \zeta_{AB}, \quad A \neq B, \end{aligned} \tag{5.4.21}$$

$$\begin{aligned} S_{AA} &= -a^2 S_0 D + V_0 S_0 A B \zeta^*_{AA} \\ S_{AB} &= S_0 V_0 A B \zeta_{AB}, \quad A \neq B, \end{aligned} \tag{5.4.22}$$

where $V_0 = \frac{4}{3}\pi a^3$ is the volume of a sink and the constants A, B, C are given by

$$\begin{aligned} A &= \frac{1}{\beta_0 a} \sinh(\beta_0 a) \\ C &= A e^{-\beta_0 a} \\ B &= \frac{3}{(\beta_0 a)^3} \left(\beta_0 a \cosh(\beta_0 a) - \sinh(\beta_0 a)\right) \\ D &= \frac{1}{3} e^{-\beta_0 a} B. \end{aligned} \tag{5.4.23}$$

using these results in (5.4.17) and taking expectation values we finally obtain

$$\langle \mathcal{H}(\bar{\pi}) \rangle = \int_V dx \left\{ \eta \frac{\bar{\pi}_2^2}{\beta_0^2} + \frac{2\bar{\pi}_2}{\beta_0^2} \frac{S_0}{V} \int dx_A \bar{\pi}_A P_A - 2(1-\eta) \frac{\bar{\pi}_2}{\beta_0^2} K' \right\}$$

$$- \int dx_A P_A \bar{\pi}_A \left\{ (-aS_0 C + S_0^2 A^2 \zeta^*_{AA}) \bar{\pi}_A + S_0^2 A^2 \int dx_B \zeta_{AB} P_{B|A} \bar{\pi}_B \right\}$$

$$- 2K' \int dx_A P_A \bar{\pi}_A \left\{ (-a^2 S_0 D + S_0 V_0 AB \zeta^*_{AA}) + S_0 V_0 AB \int dx_B \zeta_{AB} P_{B|A} + \frac{S_0}{\beta_0^2} \right\}. \tag{5.4.24}$$

The probability densities P_A, $P_{B|A}$ appearing in (5.4.24) are as defined in chapter 4.

We now take the variation of (5.4.24) with respect to $\bar{\pi}_2$ and $\bar{\pi}_A$ and set the results equal to zero to obtain two equations. Setting the variation with respect to $\bar{\pi}_2$ equal to zero implies

$$\eta \frac{\bar{\pi}_2}{\beta_0^2} + \frac{S_0}{\beta_0^2 V} \int dx_A \bar{\pi}_A P_A = (1-\eta) \frac{K'}{\beta_0^2}, \tag{5.4.25}$$

and considering the variation with respect to $\bar{\pi}_A$ gives

$$(aC - S_0 A^2 \zeta^*_{AA}) \bar{\pi}_A - S_0 A^2 \int dx_B \zeta_{AB} P_{B|A} \bar{\pi}_B + \frac{\bar{\pi}_2}{\beta_0^2}$$

$$= \frac{K'}{\beta_0^2} \left[1 - (\beta_0 a)^2 D + \beta_0^2 V_0 AB \zeta^*_{AA} + \beta_0^2 AB V_0 \int dx_B \zeta_{AB} P_{B|A} \right], \tag{5.4.26}$$

having cancelled a factor $S_0 P_A$. The integrals appearing in (5.4.26) converge when $\beta_0 R \gg 1$, R being a typical diameter of V. Also, in this limit, when x_A is not close to ∂V $G^*_{AA} \sim 0$ so that terms involving it can be neglected. We now take V to be large and the medium statistically uniform and isotropic. In this case for x_A not close to ∂V we can replace $\bar{\pi}_A$ by a constant $\bar{\pi}_1$, independent of A and use the infinite body form of the Green function.

Equations (5.4.25) and (5.4.26) now become

$$\eta\,\bar{\pi}_2 + \frac{3\eta}{a}\bar{\pi}_1 = (1-\eta)K', \tag{5.4.27}$$

and

$$\frac{\bar{\pi}_2}{(\beta_0 a)^2} + \frac{\bar{\pi}_1}{a}\left[C - 4\bar{\pi}aA^2\int dx_\beta \varphi^{\infty}_{AB}\rho_{B|a}\right] = \frac{K'}{(\beta_0 a)^2}\left[1 - (\beta_0 a)^2 D + \beta_0^2 V_0 AB\int dx_\beta \varphi^{\infty}_{AB}\rho_{B|A}\right]. \tag{5.4.28}$$

It is possible when $\beta_0 R \gg 1$ to substitute $\bar{\pi}_A = \bar{\pi}_1$, directly into (5.4.25), (5.4.26) because the Green function is well behaved: far from the source G decays exponentially. In chapter 4 we effectively considered the case $\beta_0 = 0$ and much more care was needed to obtain convergent integrals. However, it was shown that the trial fields q^A are independent of the configuration when x_A is far from ∂V.

Solutions of (5.4.27), (5.4.28) will be considered in the next section.

5.5 Self Consistent Estimates and Results

The problem we face now is the choice of a suitable comparison material. Any β_0 will provide us with estimates of k^2 through the solution of (5.4.27), (5.4.28) and the relations (5.4.8), (5.4.9), but there is no way a priori of knowing which is the best choice. However, we can obtain self consistent estimates for the sink strength by choosing the comparison medium as the overall medium. We set $\beta_0 = k$ and find from (5.4.8), (5.4.9) that the condition for self consistency is

$$\langle \bar{\pi} \rangle = 0. \tag{5.5.1}$$

This condition is directly analogous to that obtained in the context of the overall modulus problem in elastostatics.

In terms of $\bar{\pi}_1$ and $\bar{\pi}_2$, (5.5.1) implies

$$\bar{\pi}_2 + \frac{3\eta}{a}\bar{\pi}_1 = 0, \tag{5.5.2}$$

and the task now is to solve (5.4.27) and (5.4.28), invoke (5.5.2) and so obtain an implicit equation for k. The result of doing this is the equation

$$\frac{(ka)^2}{3\eta}\left[C - 4\pi a A^2 \int dx_B \zeta^{\infty}_{AB} \rho_{B|A}\right] - \left[1-(ka)^2 D + (ka)^2 AB \frac{4\pi a}{3} \int dx_B \zeta^{\infty}_{AB} \rho_{B|A}\right]$$

$$-1 = 0, \tag{5.5.3}$$

where the constants A, B, C, D are evaluated using k. The integrals in (5.5.3) can be written in terms of the pair distribution function g(x) introduced in 4.8 so that

$$\frac{4\pi a}{3} \int dx_B \zeta^{\infty}_{AB} \rho_{B|A} = -4\eta \zeta(2ak), \tag{5.5.4}$$

where

$$\zeta(t) = \int_1^{\infty} x e^{-tx} g(x)\, dx. \tag{5.5.5}$$

Equation (5.5.3) is now given explicitly as

$$e^{-ka}\left[ka \sinh(ka) + \frac{3\eta}{ka}\left(ka \cosh(ka) - \sinh(ka)\right)\right]$$

$$+ 12\eta \zeta(2ak) \sinh(ka)\left[\sinh ka + \frac{3\eta}{(ka)^2}\left(ka \cosh(ka) - \sinh(ka)\right)\right]$$

$$-6\eta = 0, \tag{5.5.6}$$

and all that remains is to define the statistics of the medium. We assume that the sinks are distributed according to the distribution of Percus and Yevick (1957) for which case G(t) was given by Wertheim (1963) as

$$\zeta(t) = \frac{t\ L(t)}{12\eta\left[L(t) + S(t) e^{t}\right]}, \tag{5.5.7}$$

where

$$L(t) = 12\eta\left[\left(1+\tfrac{1}{2}\eta\right)t + (1+2\eta)\right], \qquad (5.5.8)$$

and

$$S(t) = (1-\eta)^2 t^3 + 6\eta(1-\eta)t^2 + 18\eta^2 t - 12\eta(1+2\eta). \qquad (5.5.9)$$

The solution of (5.5.6) is displayed on figure 5.1 as the normalized flux into one void. Also shown for comparison are the lower bound derived from the Percus-Yevick distribution and the result of the simple self-consistent calculation performed in 4.2. We see that, although the results of the present calculation lie above the simple self-consistent result, at concentrations greater than about 1/3 they violate the lower bound. However, the results do display the correct asymptotic form (4.8.13) as $\eta \to 0$. Hence at low concentrations the simple self-consistent estimate would still seem to be the natural choice.

In conclusion we remark that the analysis presented in this chapter can easily be extended to deal with diffusion to aligned edge dislocations having no drift field associated with them. The present approach includes the screening effect of a large number of sinks so that it is free of the severe convergence problems which arise when the method of chapter 4 is used. However, the results of this section show that the improved self-consistent estimate is still likely to be unreliable at high concentrations.

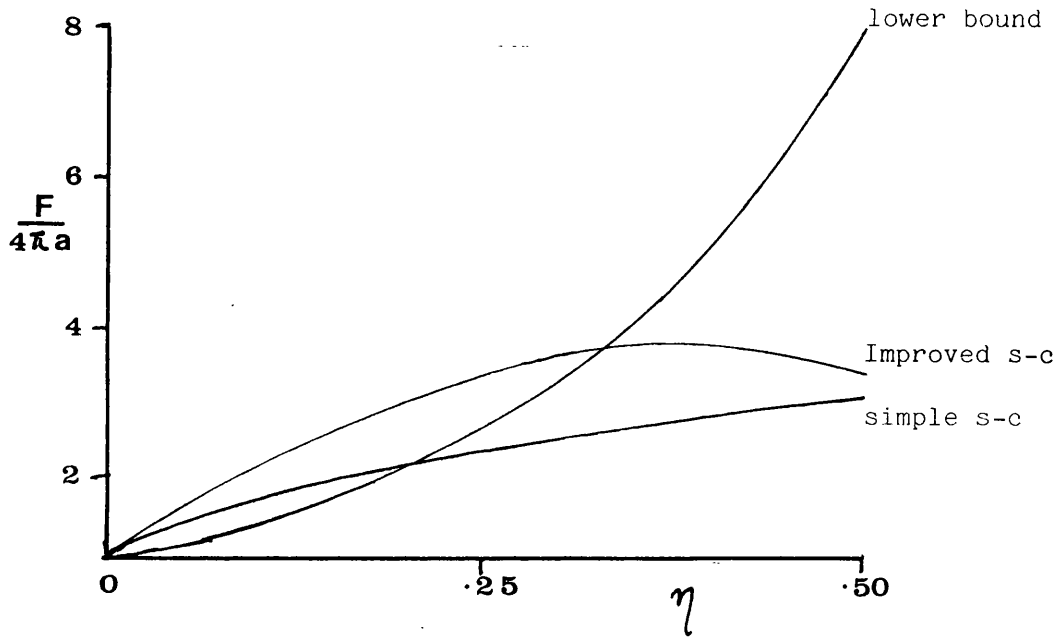


Figure 5.1 Plots of the improved self-consistent estimate and the lower bound of Chapter 4 for the Percus-Yevick model. Also shown is the simple self-consistent estimate of Chapter 4.

References

BASTECKA, J. and KROUPA, F. 1964 Czech. J. Phys. 14, 443.

BATCHELOR, G.K. and GREEN, J.T. 1972 J. Fluid Mech. 56, 401.

BENSOUSSAN, A., LIONS, J.L. and PAPANICOLAU, G. 1978 Asymptotic Analysis for Periodic Structures. Amsterdam : North-Holland.

BRAILSFORD, A.D. 1976 J. Nucl. Mat. 60, 257.

BRAILSFORD, A.D. and BULLOUGH, R. 1972 J. Nucl. Mat. 44, 121.

BRAILSFORD, A.D. and BULLOUGH, R. 1976 Vacancy 76. Proc. European Conf., University of Bristol, September 1976.

BRAILSFORD, A.D., BULLOUGH, R. and HAYNS, M.R. 1976 J. Nucl. Mat. 60, 246.

BRAILSFORD, A.D. and MAJOR, K.G. 1964 J. Appl. Phys. 15, 313.

BRINKMAN, H.C. 1947 Appl. Sci. Res. A1, 27.

BULLOUGH, R. and HAYNS, M.R. 1978 Continuum models of Discrete Systems. Proc. Int. Conf., Mont Gabriel, Quebec, June 1977, p.469. University of Waterloo Press.

BULLOUGH, R. and NEWMAN, R.C. 1970 Rep. Prog. Phys. 33, 101.

BULLOUGH, R. and PERRIN, R.C. 1971 Voids Formed by Irradiation of Reactor Materials. Proc. Conf. B.N.E.S., Reading University, March 1971, p.79. (S.F. Pugh, M.H. Loretto and D.I.R. Norris eds.)

BULLOUGH, R., WELLS, D.W., WILLIS, J.R. and WOOD, M.H. 1981 Dislocation Modelling of Physical Systems. Proc. Acta/Scripta Metallurgica Conf., Gainesville, Florida, June 1980.

CHILDRESS, S. 1972 J. Chem. Phys. 56, 2527.

DEVANEY, A.J. 1980 J. Math. Phys. 21, 2603.

DWIGHT, H.B.	1964	Tables of Integrals and Other Mathematical Data. New York, MacMillan.
FRAENKEL, L.E.	1969	Proc. Camb. Phil. Soc. 65, 263.
HANSEN, J.P. and McDONALD, I.R.	1976	Theory of Simple Liquids. London, Academic Press.
HARKNESS, S.D. and CHE-YU LI,	1971	Met. Trans. 2, 1457.
HASHIN, Z. and SHTRIKMAN, S.	1962a	J. Mech. Phys. Solids 10, 335.
HASHIN, Z. and SHTRIKMAN, S.	1962b	J. Mech. Phys. Solids 10, 343
HASHIN, Z. and SHTRIKMAN, S.	1963	J. Mech. Phys. Solids 11, 127
HEALD, P.T. and SPEIGHT, M.V.	1975	Acta Met. 23, 1389.
HILL, R.	1952	Proc. Phys. Soc. A 65, 349.
HILL, R.	1963	Progress in Applied Mechanics - The Prager Anniversary Volume, p.99. New York, MacMillan.
HINCH, E.J.	1977	J. Fluid Mech. 83, 659.
HOWELLS, I.D.	1974	J. Fluid Mech. 64, 449.
KERNER, E.H.	1956	Proc. Phys. Soc. B 69, 808.
KORRINGA, J.	1973	J. Math. Phys. 14, 509.
KRONER, E.	1977	J. Mech. Phys. Solids 25, 137.
LAX, M.	1952	Phys. Rev. 85, 621.
MARGVELASHVILI, I.G. and SARALIDZE, Z.K.	1974	Sov. Phys : Solid St. 15, 1774.
MATERN, B.	1960	Meddn St. SkogsforskInst . 49, 5, 7.
MAXWELL, J.C.	1892	A Treatise on Electricity and Magnetism. 3rd Edn., Vol. 1. Clarendon Press.
PAPANICOLAU, G.C.	1980	Transactions of the twenty-fifth Conference of Army Mathematicians ARO Report 80-1.
PERCUS, J.K. and YEVICK, G.J.	1957	Phys. Rev. 110, 1.

SIEDMAN, D.N. and BALLUFFI, R.W.	1966	Phil. Mag. 13, 649.
TALBOT, D.R.S. and WILLIS, J.R.	1980	Proc. R. Soc. Lond. A 370, 351.
THROOP, G.J. and BEARMAN, R.J.	1964	J. Chem. Phys. 42, 2408.
VAN DYKE, J.D.	1964	Perturbation Methods in Fluid Mechanics, New York, Academic Press.
VARADAN, V.K., VARADAN, V.V. and PAO, Y.-H.	1978	J. Acoust. Soc. Am. 63, 1310
WERTHEIM, M.S.	1963	Phys. Rev. Lett. 10, 321.
WILLIS, J.R. and ACTON, J.R.	1976	Q. Jl. Mech. appl. Math. 29, 163.
WILLIS, J.R.	1977	J. Mech. Phys. Solids 25, 185.
WILLIS, J.R.	1978	Continuum Models of Discrete Systems. Proc. Int. Conf., Mont Gabriel, Quebec, June 1977, p. 185. University of Waterloo Press.
WILLIS, J.R.	1979	Variational Methods in Mechanics of Solids. Proc. Int. Conf., Northwestern University, September 1978. Pergamon Press.
WILLIS, J.R.	1980	J. Mech. Phys. Solids 28, 287.
WILLIS. J.R.	1981a	Wave Motion 3, 1.
WILLIS, J.R.	1981b	Mechanics of Solids, the Rodney Hill Sixtieth Anniversary Volume (H.G. Hopkins and M.J. Sewell eds.), p. 653. Pergamon Press (to appear).

Proc. R. Soc. Lond. A **370**, 351–374 (1980)
Printed in Great Britain

The effective sink strength of a random array of voids in irradiated material

BY D. R. S. TALBOT AND J. R. WILLIS
School of Mathematics, University of Bath, Claverton Down, Bath, BA2 7AY U.K.

(*Communicated by Rodney Hill, F.R.S. – Received* 14 *June* 1979)

The mean sink strength of a distribution of voids in a solid containing a diffusing population of defects is defined unambiguously in terms of the spatial average of the solution of a particular steady-state diffusion problem. A variational characterization of this problem then leads to lower bounds for the sink strength. The voids are supposed to be distributed according to some stochastic process; this feature is incorporated by extremizing the expectation value of the variational functional with respect to simple configuration-dependent trial fields. This results in bounds for the sink strength which involve correlations between small numbers of voids. The bounds are highly sensitive to the statistics of the void distribution and in fact, may in some cases demonstrate that a postulated correlation function is inconceivable as a result of any stochastic mixing process. This occurs for the 'well-stirred' approximation, at a volume concentration around 0.2, at which the strict lower bound becomes infinite, corresponding to the expectation of a quadratic functional known to be definite becoming indefinite. Results are compared with those obtained from a self-consistent calculation and from small-concentration perturbation theory. It is demonstrated that a suitably constructed version of the latter yields a strict lower bound which can actually exceed the self-consistent estimate at high concentrations. In such cases, therefore, it is the more reliable.

1. INTRODUCTION

An important problem associated with the operation of nuclear reactors concerns the prediction of the swelling of components (both fuel elements and certain structural members) induced by the irradiation, during both normal and abnormal operating conditions: a recent review has been given by Bullough & Hayns (1978). The swelling may occur because fission gas is generated in the component in question, resulting in the formation of gas bubbles which then act as sinks for any subsequently generated gas. Additionally, the irradiation may 'damage' the material by displacing atoms, so creating equal numbers of vacancies and interstitials, which then rearrange themselves by diffusion. A variety of sinks for these defects will exist in the material including, in addition to gas bubbles or voids, precipitate

surfaces, grain boundaries and dislocations; the relative efficiency of these competing sinks determines the growth of the gas bubbles or voids and so determines the rate of swelling.

The detailed modelling of these processes is a formidable task requiring, in general, the solution of a set of coupled nonlinear diffusion equations in the presence of a microstructure whose evolution in time is to be found as part of the solution. The problem has some features in common with the description of chemical reactions and it is usual to apply to it a simplifying approximation which is usually described as 'chemical rate theory'. In this, at any given instant, the microstructure is modelled by continuous distributions of sinks whose strengths are related to the parameters that describe them (void radius, void density, dislocation density, etc.), from a set of simple 'self-consistent' calculations; an elementary example is presented explicitly in § 2 below. The flux of defects into each type of sink is then determined from the diffuson equations and this, in turn, determines the evolution of the sinks. The nucleation and growth of a population of gas bubbles has been treated in this way, for example, by Hayns & Bullough (1975).

The purpose of the present work is to consider, more rigorously than the self-consistent method allows, the problem of estimating sink strengths. This is done through a detailed study of a very simple model problem, which involves a random distribution of identical spherical voids acting as sinks for just one diffusing population of defects (which may be thought of as gas, to be definite), when no other competing sinks are present. Brailsford (1976) has considered the same problem, but only from the standpoint of perturbation theory, valid in the limit of a low concentration of voids. Here, we begin by formulating a problem exactly for a finite body containing a specified distribution of voids and then give a precise definition of the effective sink strength for that distribution, analogous to the definition of the overall elastic moduli of a composite given by Hill (1952). An integral equation formulaton for the boundary value is then given, which is similar in general terms to that employed in the 'overall modulus' problem by Willis & Acton (1976) and Willis (1977, 1978). In contrast to the overall modulus problem, however, it is impossible to secure integrals that are guaranteed to converge, so that the development has to proceed in the context of a finite body, with explicit allowance for boundary effects. Estimates of the sink strength are found from a variational principle, sketched briefly by Willis (1978), which is somewhat analogous to the variational principle of Hashin & Shtrikman (1962*a*, *b*; 1963) for the 'overall modulus' problem. Lower bounds to the effective sink strength are found by substituting simple configuration-dependent trial fields into the variational fuctional, ensemble averaging and then extremizing. Although allowance for the boundary of the finite body is essential, the body can at this stage be taken large and uniformity is obtained, except in a boundary layer.

The results of the variational formulation can be related to a perturbation expansion of the solution of the integral equation, similar to the one given by Brailsford (1976). It emerges, interestingly, that the simplest approximation which, if derived

from perturbation theory, has validity only at low concentrations, in fact provides a strict lower bound, valid at any concentration. Examples demonstrate the extreme sensitivity of the bound to the statistics of the distribution of the voids. The self-consistent approximation lacks this sensitivity and pair correlation functions are displayed for which the rigorous lower bound exceeds the self-consistent estimate at high concentrations of voids; this is in contrast to the situation when overall moduli are calculated, for which the usual self-consistent estimates always lie between the Hashin–Shtrikman bounds (see, for example, Kröner (1977) or Willis (1977)). In fact, the sensitivity is such that an apparent lower bound that is obtained by use of the so-called 'well-stirred' approximation actually becomes infinite at a volume concentration of voids around 0.2; this approximation is therefore inconceivable as a result of any stochastic mixing process, at least at high concentrations. Plainly, therefore postulated pair correlation functions must satisfy some set of conditions (of which finiteness of our bound is an example) but a complete set of necessary and sufficient conditions is at present unknown. Reassuringly, bounds that are obtained for distributions obtained from the stochastic models of Matérn (1960), and also from the approximation of Percus and Yevick (1957) for a statistical mechanical distribution of hard spheres, are well behaved. They reduce to the well-stirred approximation in the limit of low concentrations; it is in this limit that the approximation has been used by Batchelor & Green (1972), Willis & Acton (1976) and others.

It should, perhaps be remarked at this point that the problem to be considered in this work is rather directly analogous to that of finding the drag exerted on a viscous fluid by a random array of spherical obstacles. The perturbation theory referred to above is closely related to that developed by Childress (1972) and Hinch (1977) for example, and the simple self-consistent calculation is analogous to one performed by Brinkman (1947). The present variational approach has not been applied to this problem, however, and it might be worthwhile to consider its extension to this and other related problems in the future.

2. Formulation of the problem

A body occupies a region V, with boundary ∂V. It contains exactly N spherical voids each of radius a, with centres at $x_A (A = 1, 2 \ldots N)$. Defects (e.g. atoms of insoluble gas) are introduced at a rate $K(x, t)$ per unit volume, throughout the region $V - V_v$, where V_v denotes the part of V occupied by the voids. The defects distribute themselves by diffusion, so that their concentration $c(x, t)$ is described by the equation

$$\partial c/\partial t = D\nabla^2 c + K(x, t), \quad x \in V - V_v, \tag{2.1}$$

together with appropriate boundary conditions. If no flux is admitted across ∂V, then

$$\partial c/\partial n = 0, \quad x \in \partial V \tag{2.2}$$

and the voids act as the only sinks for the defects. The simplest boundary condition that can be applied at the void surfaces is

$$c = 0 \quad x \in \partial V_v; \tag{2.3}$$

this will be adopted in the sequel. The problem described by equations (2.1) to (2.3) is a complex one if N is large, even if possible growth of the voids is not admitted, and it is generally assumed that equations (2.1) and (2.3) can be replaced by a single 'homogenized' equation

$$\partial c/\partial t = \hat{D}(\nabla^2 c - k^2 c) + \hat{K}(x, t), \quad x \in V, \tag{2.4}$$

in which $\hat{K}$ is some smoothed-out version of K (in a real situation K is unlikely to be known in any case), the distribution of voids is modelled by a continuous distribution of sinks of strength k^2 per unit volume, and $\hat{D}$ is some 'overall' diffusion coefficient, usually (but perhaps incorrectly) identified with D. The boundary condition (2.2) is, of course, retained.

No attempt will be made in the present work to justify the replacement of (2.1) and (2.3) by (2.4). It may be remarked, however, that if the replacement is to succeed generally, then it must do so in particular under steady-state conditions, with K uniform throughout $V - V_v$. Equation (2.2) then reduces to the form

$$\nabla^2 c + K/D = 0, \quad x \in V - V_v, \tag{2.5}$$

while (2.4) becomes

$$\nabla^2 c - k^2 c + \hat{K}/\hat{D} = 0, \quad x \in V, \tag{2.6}$$

where $\hat{K} = K(1-\eta)$, η representing the volume ratio occupied by the voids. Equation (2.6), with the boundary condition (2.2), has the solution

$$c = \bar{c} = \hat{K}/(\hat{D}k^2). \tag{2.7}$$

The problem thus reduces to calculating, from the solution of (2.2), (2.3) and (2.5), the mean value $\bar{c}$ of c, defined by

$$\bar{c} = \frac{1}{V}\int_{V-V_v} c \, \mathrm{d}x \tag{2.8}$$

(V also being used to denote the volume of the region, to avoid excessive notation). Imposing the minimal requirement of consistency of (2.7) and (2.8) now yields the relation

$$(\hat{D}k^2)\bar{c} = K(1-\eta), \tag{2.9}$$

which will be taken to define $(\hat{D}k^2)$.

Mathematically, the problem is closely related to that of determining the drag exerted by a set of fixed spheres on a viscous fluid: the concentration c is analogous to fluid velocity and the sink term $\hat{D}k^2 c$ in (2.4) is analogous to Darcy resistance. Of course, for a complete description a proper estimate for $\hat{D}$ is required, but the problem of finding such an estimate is not considered here.

Before we discuss further the system (2.2), (2.3) and (2.5), it is convenient to consider a simpler, but inexact, way of estimating k^2, and hence $\hat{D}k^2$ if $\hat{D}$ is identified

with D. More complicated variants are easy to devise but, in its simplest form, k^2 is estimated by inserting one spherical void in a medium containing a continuous distribution of sinks, so that

$$\nabla^2 c - k^2 c + k^2 = 0, \quad |x| > a, \tag{2.10}$$

with $c = 0$ when $|x| = a$ (the source having been normalized so that $\bar{c} = 1$). The appropriate solution of equation (2.10) is

$$c = 1 - (a/r)\,\mathrm{e}^{-k(r-a)}, \tag{2.11}$$

where $r = |x|$, so that the flux (normalized so that $\hat{D} = 1$) into the void is given as

$$F = 4\pi a(1 + ka). \tag{2.12}$$

If, now, the actual voids are distributed at number density $n = N/V$ (so that $\eta = \frac{4}{3}\pi n a^3$), the requirement of self-consistency generates the equation

$$k^2 = nF = 4\pi a n(1 + ka) \tag{2.13}$$

for k. The great advantage of this method of estimating k is its simplicity: plainly, it can be refined to allow for different boundary conditions, sink-free regions, etc., and can also be extended to estimate the effective strengths of competing types of sink in the same medium (Bullough & Hayns 1978). Its drawback is that it allows only qualitatively for the distribution of the voids. The remainder of this work is devoted to obtaining more rigorous estimates of $(\hat{D}k^2)$ which make explicit allowance for this distribution.

3. An integral equation and associated variational principle

The problem defined by equation (2.5), together with the boundary conditions (2.2) and (2.3), will now be expressed in the form of an integral equation. To this end, a Green function for the region V is defined by the equations

$$\nabla^2 G(x, x') = \delta(x - x') - 1/V, \quad x \in V, \tag{3.1}$$

$$(\partial G/\partial n)(x, x') = 0, \quad x \in \partial V, \tag{3.2}$$

in which the right side of (3.1) satisfies the 'no net source' condition required for consistency with (3.2). The solution of (3.1), (3.2) is made unique by requiring that

$$\int_V G(x, x')\,\mathrm{d}x = 0 \tag{3.3}$$

which, incidently, ensures that $G(x, x') = G(x', x)$. Application of Green's theorem over the region $V - V_\mathrm{v}$ now gives

$$c(x') - \bar{c} = \int_{\partial V_\mathrm{v}} G(x, x')\,q(x)\,\mathrm{d}s - K' \int_{V - V_\mathrm{v}} G(x, x')\,\mathrm{d}x, \; x' \in V - V_\mathrm{v}, \tag{3.4}$$

where

$$q(x) = \partial c(x)/\partial n, \quad x \in \partial V_{\mathrm{v}} \tag{3.5}$$

and

$$K' = K/D. \tag{3.6}$$

The boundary condition (2.3) now yields the equation

$$\int_{\partial V_{\mathrm{v}}} G(x, x')\, q(x)\, \mathrm{d}s - K' \int_{V - V_{\mathrm{v}}} G(x, x')\, \mathrm{d}x + \bar{c} = 0, \quad x' \in \partial V_{\mathrm{v}}, \tag{3.7}$$

in which, for consistency,

$$(V - V_{\mathrm{v}})\, K' = \int_{\partial V_{\mathrm{v}}} q(x)\, \mathrm{d}s. \tag{3.8}$$

The problem is to find $\bar{c}$ given K' or, equivalently, because the problem is linear, to find K' given $\bar{c}$. With the latter interpretation, equation (3.7), together with (3.8), becomes an integral equation for $q(x')$. Before proceeding with its solution it may be noted that, when $x' \in V_{\mathrm{v}}$, equation (3.4) defines a function $c(x')$ which is harmonic and therefore zero within V_{v}; the integral equation formulation thus has some similarity with Howells's (1974) formulation of the 'viscous drag' problem, in which the velocity field was defined to be zero throughout the volume occupied by the spheres. There is also a similarity with the Hashin-Shtrikman formulation of the 'overall modulus' problem, in which a 'polarized' homogeneous comparison material is employed: the field $c(x')$ of the present problem would be generated in a homogeneous medium if sinks $q(x)$ were introduced over ∂V_{v}. The sinks $q(x)$ are thus in approximate correspondence with the 'polarization' and equation (3.7) corresponds to an integral equation for the polarization considered, for example, by Korringa (1973), Willis & Acton (1976) and Willis (1977).

To motivate the construction to follow, consider, instead of (3.7) and (3.8), the integral equation

$$\int_{V'} G(x, x') f(x)\, \mathrm{d}x + g(x') = 0, \quad x' \in V' \subset V, \tag{3.9}$$

where V' is some subregion of V. It has been noted already that $G(x, x')$ is symmetric in x and x' and it is easy to prove that, for any function f^* defined on V',

$$\int_{V'} \mathrm{d}x' f^*(x') \int_{V'} \mathrm{d}x\, G(x, x') f^*(x) \leqslant 0. \tag{3.10}$$

It follows, therefore that (3.9) is equivalent to the maximum principle

$$\frac{1}{V} \int_{V'} \mathrm{d}x' f^*(x') \int_{V'} \mathrm{d}x\, G(x, x') f^*(x) + \frac{2}{V} \int_{V'} \mathrm{d}x' f^*(x')\, g(x') \leqslant \frac{1}{V} \int_{V'} \mathrm{d}x' f(x')\, g(x'), \tag{3.11}$$

for any approximation f^* to f. Since equation (3.7) holds for $x' \in V_{\mathrm{v}}$ if it does for

$x' \in \partial V_v$, it can be shown similarly that equations (3.7) and (3.8) are equivalent to the maximum principle

$$\frac{1}{V}\left\{\int_{\partial V_v} ds'\, q^*(x') + K^* \int_{V_v} dx'\right\}\left\{\int_{\partial V_v} ds\, G(x, x')\, q^*(x') + K^* \int_{V_v} dx\, G(x, x') + 2\bar{c}\right\} \leqslant K'\bar{c}, \quad (3.12)$$

use being made of the property (3.3) that G has zero mean value to replace an integral over $V - V_v$ by one over V_v. In (3.12), q^* is any function defined on ∂V_v and K^* is the corresponding estimate for K':

$$K^* = \frac{1}{V(1-\eta)} \int_{\partial V_v} q^*(x)\, ds. \quad (3.13)$$

The maximum principle (3.12) provides a ready source of precise information upon the overall sink strength $\hat{D}k^2$: for any choice of q^*, it generates a lower bound for K' and so, through (2.9), a strict lower bound to $\hat{D}k^2$.

Approximations q^* will be considered in the sequel, which are constant over the surface of any sphere. If the region occupied by sphere A is denoted by V_A, with surface ∂V_A, q^* will be taken to have the form

$$q^*(x) = q^A, \quad x \in \partial V_A, \quad A = 1, 2, \ldots, N, \quad (3.14)$$

where $q^A (A = 1, 2, \ldots, N)$ are constants. Then, (3.12) gives

$$\frac{1}{V}\sum_A \left\{\int_{\partial V_A} ds' q^A + K^* \int_{V_A} dx'\right\}\left\{\int_{\partial V_A} ds G(x, x')\, q^A + K^* \int_{V_A} dx\, G(x, x') + \sum_{B \neq A}\left[\int_{\partial V_B} ds\, G(x, x')\, q^B + K^* \int_{V_B} dx\, G(x, x)\right] + 2\bar{c}\right\} \leqslant K'\bar{c}, \quad (3.15)$$

where

$$K^* = \frac{4\pi a^2}{V(1-\eta)} \sum_A q^A. \quad (3.16)$$

Now when x' lies within V_A or else on its surface ∂V_A, and x is within V_B or on ∂V_B, $G(x, x')$ can be expressed in the form

$$G(x, x') = -|x - x_B|^2/6V + G_1(x, x'), \quad (3.17)$$

for some function G_1 which is harmonic in x, with $G_1(x_B, x') = G(x_B, x')$. The mean value theorem therefore gives

$$\int_{\partial V_B} G(x, x')\, ds = 4\pi a^2 G(x_B, x') - 2\pi a^4/3V \quad (3.18)$$

and

$$\int_{V_B} G(x, x')\, dx = \frac{4\pi a^3}{3} G(x_B, x') - \frac{2\pi a^5}{15V}. \quad (3.19)$$

Also, when both x and x' are within or close to V_A,

$$G(x,x') = -\frac{1}{4\pi|x-x'|} - \frac{|x-x_A|^2}{6V} + G_A(x,x'), \tag{3.20}$$

for some function G_A which is harmonic in x, and it follows that

$$\int_{\partial V_A} G(x,x')\,\mathrm{d}s = -a - \frac{2\pi a^4}{3V} + 4\pi a^2 G_A(x_A,x'),\ x' \in V_A \tag{3.21}$$

and

$$\int_{V_A} G(x,x')\,\mathrm{d}s = -\frac{a^2}{2} + \frac{|x'-x_A|^2}{6} - \frac{2\pi a^5}{15V} + \frac{4\pi a^3}{3} G_A(x_A,x'),\ x' \in V_A. \tag{3.22}$$

The results (3.18), (3.19), (3.21) and (3.22) may be substituted into (3.15) and then used again to reduce the integrals over x' (remembering that $G_A(x_A,x')$ is not harmonic in x' but instead has a representation like (3.17)). Use of (3.16), together with the relation $\eta = 4\pi a^3 N/3V$, leads finally to the inequality

$$\frac{1}{V}\sum_A (4\pi a^2 q^A + \tfrac{4}{3}\pi a^3 K^*)\left[\left(\frac{-a+4\pi a^2 G_A}{4\pi a^2}\right)(4\pi a^2 q^A + \tfrac{4}{3}\pi a^3 K^*) + \sum_{B\neq A} G_{AB}(4\pi a^2 q^B + \tfrac{4}{3}\pi a^3 K^*)\right] - \frac{a^2}{15}(5-\eta)(K^*)^2 + 2K^*\bar{c} \leqslant K'\bar{c}, \tag{3.23}$$

where G_A here denotes $G_A(x_A,x_A)$ and G_{AB} denotes $G(x_A,x_B)$. Explicit bounds for K', valid when V is large and the voids are located only stochastically will be developed from (3.23) in the following sections.

4. Description of the random medium

If the positions of the N voids were known with precision (for example, if they were distributed on a lattice), the inequality (3.23) could be used immediately to provide a bound for K' which, furthermore, could be optimized by allowing the N constants q^A to vary. Although the particular problem studied here has not been analyzed for periodic arrays of voids there is, in fact, an extensive literature on homogenization for similar problems (see, for example, Bensoussan *et al.* 1978). The present work will therefore focus upon a class of media in which the voids are distributed randomly, in a sense described informally below. The actual medium (for which, of course, the precise location of every void could in principle be determined) is regarded as one taken from an ensemble of media, labelled by some parameter α from a sample space $\mathscr{S}$ over which a probability density $P(\alpha)$ is defined. The probability density P_A for finding a void centred at x_A is then defined from the requirement that, for any subset U of V, the expected number of voids centred in U is $\int_U P_A\,\mathrm{d}x_A$. Thus,

$$\int_U P_A\,\mathrm{d}x_A = \sum_{k=1}^{N} k \int_{\mathscr{S}_{U(k)}} P(\alpha)\,\mathrm{d}\alpha, \tag{4.1}$$

where $\mathscr{S}_{U(k)}$ represents the subset of $\mathscr{S}$ for which there are exactly k voids centred in U. Since, plainly, $\mathscr{S}_{V(k)} = \mathscr{S}$ if $k = N$ and is empty otherwise, equation (4.1) implies

$$\int_V P_A \, \mathrm{d}x_A = N, \tag{4.2}$$

as it should. Similarly, the joint probability density P_{AB} for finding distinct voids centred at x_A and x_B is defined so that, for disjoint subsets U and W of V, the expected value of the product of the number of voids centred in U with the number centred in W is

$$\int_U \mathrm{d}x_A \int_W \mathrm{d}x_B \, P_{AB};$$

thus

$$\int_U \mathrm{d}x_A \int_W \mathrm{d}x_B \, P_{AB} = \sum_{k=1}^{N-1} \sum_{l=1}^{N-k} kl \int_{\mathscr{S}_{U(k)W(l)}} P(\alpha) \, \mathrm{d}\alpha, \tag{4.3}$$

where $\mathscr{S}_{U(k)W(l)}$ is the subset of $\mathscr{S}$ for which there are k voids in U and l voids in W. If U is so small that it can contain at most one void, and if $W = V - U$, then $\mathscr{S}_{U(k)W(l)} = \mathscr{S}_{U(k)}$ if $l = N - k$ and $k = 0$ or 1 and is empty otherwise. In this case, therefore,

$$\int_U \mathrm{d}x_A \int_W \mathrm{d}x_B \, P_{AB} = (N-1) \int_{\mathscr{S}_{U(1)}} P(\alpha) \, \mathrm{d}\alpha = (N-1) \int_U P_A \, \mathrm{d}x_A. \tag{4.4}$$

If the conditional density $P_{B|A}$ is now defined by the relation

$$P_{AB} = P_{B|A} P_A \tag{4.5}$$

(with $P_{A|A} = 0$), equation (4.4) implies

$$\int_V P_{B|A} \, \mathrm{d}x_B = (N-1), \tag{4.6}$$

which states that if there is a void at x_A, then there must be exactly $N-1$ others in V. Higher-order densities will be defined similarly: $P_{ABCD\ldots}$ will denote the joint probability density for finding voids centred at x_A, x_B, x_C, $x_D\ldots$, and $P_{AB\ldots|CD\ldots}$ will denote the joint probability density for finding voids centred at $x_A, x_B\ldots$, given that voids are centred at x_C, $x_D\ldots$. For either, the voids are always assumed distinct, so that a repeated suffix will always imply that the density is zero.

It has been assumed implicitly in the above that the voids cannot overlap, that is, that the model is of the 'hard-core' type. Otherwise, the description is fairly general. For the work to follow, however, some further assumptions will be made. First, the limiting case of a large region V will be considered, with the number density $n = N/V$ remaining finite. Also, in this limit, it will be assumed that the distribution of voids is statistically uniform, in the sense that $P_{AB\ldots}$ is insensitive to rigid translations of the points x_A, $x_B\ldots$, except when one or more of the points is close to ∂V, and statistically isotropic, in the sense that $P_{AB\ldots}$ is insensitive to rigid

rotations of x_A, x_B..., again except when some point is close to ∂V. This implies, in particular, that $P_A \sim n$ except when x_A is close to ∂V. A further assumption that will be made is that there is no long-range order, in the sense that

$$P_{AB\ldots\,CD\ldots} \sim P_{AB\ldots} P_{CD\ldots} \tag{4.7}$$

when the points $(x_A, x_B, \ldots)$ are far from the points $(x_C, x_D, \ldots)$, even when some points may be close to ∂V. Exact conditions under which a process for generating a random medium realizes the above assumptions are unknown. Also, it will emerge later that some initially plausible functions P_{AB} generate results that are untenable and so presumably cannot be realized for any hard-core model. Again, however, systematic necessary restrictions are not yet known.

5. A simple lower bound for K′

Given a particular realization of the random medium with parameter α, the position of each void is specified and solution of the integral equation (3.7) would yield a value $K'(\alpha)$ for K', which would depend upon α. It seems plausible, however, that, if V is large and the medium correspondingly statistically uniform, $K'(\alpha)$ should become asymptotically independent of α, and so coincide with its expectation value

$$\langle K' \rangle = \int_{\mathscr{S}} K(\alpha) P(\alpha)\, d\alpha. \tag{5.1}$$

Dually, if $\langle K' \rangle$ is calculated for a finite region V, then it might be expected that $\langle K' \rangle$ tends to a well-defined limit as V becomes large. The object of this section will be to develop a simple lower bound for $\langle K' \rangle$, in the limit of large V. The bound is obtained by allowing q^A in the inequality (3.23) to depend just upon the position x_A of the sphere A, taking expectations of (3.23) and then optimizing the function $q^A = q^A(x_A)$. In view of the assumed statistical uniformity, it might be expected that the optimal q^A should be a constant q^0, independent of x_A. This will indeed be borne out in what follows, except when x_A is close to ∂V. It will appear, however, that substitution of $q^A = q^0$ directly into (3.23) even in the boundary layer leads to a useful answer only if the joint probability P_{AB} has some special (and generally implausible) properties, the Green function being sufficiently badly behaved for the contribution from the boundary layer to render the bound useless in the general case. This contrasts with the situation in 'overall modulus' theory, in which a piecewise-constant polarization can be substituted directly into the variational principle analogous to (3.23), with negligible perturbation from the boundary layer when V is large (Willis 1977).

Proceeding now to details, the expectation value of the left side of (3.23) is maximized by setting its variation with respect to q^R equal to zero. It is easy to check, in fact, that the variation may be obtained by differentiating the left side of (3.23) with respect to q^R and then taking the conditional expectation, with x_R fixed.

Taking account of the definition (3.16) for K^* and the symmetry of G_{AB}, the required derivative is readily found to be $(2/V)$ times the following expression:

$$4\pi a^2\left\{\left(\frac{-a+4\pi a^2 G_R}{4\pi a^2}\right)(4\pi a^2 q^R+\tfrac{4}{3}\pi a^3 \mathrm{K}^*)+\sum_{B\neq R} G_{RB}(4\pi a^2 q^B+\tfrac{4}{3}\pi a^2 K^*)\right\}$$
$$+(\tfrac{4}{3}\pi a^3)\left(\frac{4\pi a^2}{V(1-\eta)}\right)\sum_A\left\{\left(\frac{-a+4\pi a^2 G_A}{4\pi a^2}\right)(4\pi a^2 q^A+\tfrac{4}{3}\pi a^3 K^*)\right.$$
$$\left.+\sum_{B\neq A} G_{AB}(4\pi a^2 q^B+\tfrac{4}{3}\pi a^3 K^*)\right\}-\frac{4\pi a^4(5-\eta)}{15(1-\eta)}K^*+\frac{4\pi a^2}{1-\eta}\bar{c}. \quad (5.2)$$

Taking the expectation value with x_R fixed is a little complicated because the suffix R must be remove explicitly from every summation. If we anticipate the form of the final result when V is large, however, the expression is much simplified if the conditional expectation of any mean value (that is, V^{-1} times a summation) is taken to coincide with is unconditional expectation value. In that case, if we set

$$\phi_R=\left(\frac{-a+4\pi a^2 G_R}{4\pi a^2}\right)(4\pi a^2 q^R+\tfrac{4}{3}\pi a^3\langle K^*\rangle)+\int G_{RB}P_{B|R}$$
$$(4\pi a^2 q^B+\tfrac{4}{3}\pi a^3\langle K^*\rangle)\,\mathrm{d}x_B, \quad (5.3)$$

where $\langle K^*\rangle$ denotes the unconditional expectation value of K^*, the conditional expectation value of (5.2) approximates to

$$4\pi a^2\phi_R+\tfrac{4}{3}\pi a^3\frac{4\pi a^2}{V(1-\eta)}\int\phi_A P_A\,\mathrm{d}x_A-\frac{4\pi a^4(5-\eta)}{15(1-\eta)}\langle K^*\rangle+\frac{4\pi a^2}{1-\eta}\bar{c}. \quad (5.4)$$

Setting this to zero shows that ϕ_R is independent of R so that the integral in (5.4) can be evaluated by (4.2). Use of the relation $\eta=4\pi a^3 N/3V$ now gives the simple equation

$$\phi_R-\tfrac{1}{15}a^2(5-\eta)\langle K^*\rangle+\bar{c}=0. \quad (5.5)$$

To proceed further, set

$$q^A=(1-\eta)a\langle K^*\rangle/3\eta+\mathrm{e}^A, \quad (5.6)$$

where

$$\int \mathrm{e}^A P_A\,\mathrm{d}x_A=0, \quad (5.7)$$

consistently with (3.16). Equation (5.5) may now be written in the form

$$\left(\frac{a\langle K^*\rangle}{3\eta}\right)\left\{(-a+4\pi a^2 G_R)+4\pi a^2\int G_{RB}P_{B|R}\,dx_B\right\}$$
$$+\mathrm{e}^R(-a+4\pi a^2 G_R)+4\pi a^2\int G_{RB}P_{B|R}\mathrm{e}^B\,\mathrm{d}x_B-\tfrac{1}{15}a^2(5-\eta)\langle K^*\rangle+\bar{c}=0 \quad (5.8)$$

or, regrouping terms,

$$(-a+4\pi a^2 G_R)\left(\frac{a}{3\eta}\langle K^*\rangle+\mathrm{e}^R\right)+4\pi a^2\int G_{RB}\left(\frac{a}{3\eta}\langle K^*\rangle+\mathrm{e}^B\right)(P_{B|R}-P_B)\,dx_B$$
$$+4\pi a^2\int G_{RB}\left(\frac{a}{3\eta}\langle K^*\rangle(P_B-n)+\mathrm{e}^B P_B\right)\mathrm{d}x_B-\tfrac{1}{15}a^2(5-\eta)\langle K^*\rangle+\bar{c}=0 \quad (5.9)$$

having also used that G has zero mean value to replace P_B by $(P_B - n)$. The assumption of no long range order ensures (with some restriction on the rate of decay of $P_{B|R} - P_B$) that the first integral in (5.9) remains finite as V becomes large. Therefore, except when x_R is close to ∂V (when G_R may be large), the second integral must be finite: this implies

$$(a/3\eta)\langle K^* \rangle (P_B - n) + \mathrm{e}^B P_B \sim 0 \tag{5.10}$$

except, perhaps when x_B lies in a boundary layer close to ∂V, across which the left side of (5.10) should have a small mean value. Since $P_B - n \sim 0$ except in the boundary layer, it follows that $\mathrm{e}^B \sim 0$ so that q^B is constant except close to ∂V. Then, when x_R is not in the boundary layer, equation (5.9) simplifies to

$$\frac{a}{3\eta}\langle K^* \rangle \left\{ -a + 4\pi a^2 \int G_{RB}(P_{B|R} - P_B)\, \mathrm{d}x_B \right\} - \tfrac{1}{15} a^2 (5 - \eta)\langle K^* \rangle + \bar{c}$$
$$+ 4\pi a^2 \int G_{RB} \left[\frac{a}{3\eta}\langle K^* \rangle (P_B - n) + \mathrm{e}^B P_B \right] \mathrm{d}x_B = 0, \tag{5.11}$$

since $G_R \sim 0$ and $\mathrm{e}^R \sim 0$. The first integral in (5.11) is independent of x_R when V is large because $(P_{B|R} - P_B)$ is insensitive to translations and, because the integral converges, G_{RB} may be replaced by its infinite body form

$$G_{RB} \sim -\frac{1}{4\pi |x_B - x_R|}. \tag{5.12}$$

Therefore, the last integral is not only finite but independent of x_R and hence zero, since its mean value over x_R is zero, by (3.3). Hence, finally, the equation

$$\frac{a^2}{3\eta}\langle K^* \rangle \left\{ 1 + a \int \frac{(P_{B|R} - P_B)}{|x_B - x_R|}\, \mathrm{d}x_B + \tfrac{1}{5}\eta(5 - \eta) \right\} = \bar{c} \tag{5.13}$$

defines $\langle K^* \rangle$ as a lower bound for $\langle K' \rangle$.

It should be noted that, had q^A been taken independent of x_A from the outset, the terms involving e^B would have been absent from (5.9) and that equation would then have been dominated by the term

$$4\pi a^2 (\tfrac{1}{3} a \langle K^* \rangle) \int (P_B - n)\, G_{RB}\, \mathrm{d}x_B. \tag{5.14}$$

It is quite conceivable that, close to ∂V, P_B might differ greatly from n: for instance, it might be exactly zero. Then, since G_{RB} would be of the order of d^{-1}, where d is a typical diameter of V, the term (5.14) would be of order d times the thickness of the boundary layer and so would become indefinitely large with V. This point was overlooked in an earlier derivation of (5.13) by Willis (1978), whose reasoning correspondingly was strictly valid only for a special (and generally unrealistic) class of distributions P_B.

An exact reduction of (5.2) has, in fact, been performed: the calculations are laborious and lead to modifications to (5.9) that are significant only in the boundary layer. The term highlighted in equation (5.10) remains the dominant feature, and (5.13) survives unchanged.

6. Interactions

An improved bound for $\langle K' \rangle$ may be sought by adopting the form

$$q^A = r^A + \sum_{B \neq A} f^{AB} \tag{6.1}$$

for q^A in (3.23), which allows for pairwise interactions. In (6.1), r^A depends upon x_A and f^{AB} depends upon both x_A and x_B. Clearly, for any given q^A, the resolution (6.1) is not unique but in the limit of large V, it can be made to by requiring that $f^{AB} \to 0$ as $|x_B - x_A| \to \infty$. For finite V, there is no objection to substituting (6.1) into (3.23) and optimizing; there will simply be no unique maximizer unless further conditions are imposed. Following the scheme outlined in Section 5, (6.1) is substituted into (3.23) and the expectation value of the result is optimized. The required variational equations are obtained by differentiating with respect to r^R and taking the expectation of the result conditional upon x_R being fixed, and differentiating with respect to f^{RS} and taking the expectation of the result with x_R and x_S fixed. Now from (6.1),

$$\frac{\partial q^A}{\partial r^R} = \frac{\partial q^A}{\partial f^{RS}} = \delta_{AR}. \tag{6.2}$$

Also, from (3.16)

$$K^* = \frac{4\pi a^2}{V(1-\eta)} \sum_A \left[r^A + \sum_{B \neq A} f^{AB} \right] \tag{6.3}$$

so that

$$\frac{\partial K^*}{\partial r^R} = \frac{\partial K^*}{\partial f^{RS}} = \frac{4\pi a^2}{V(1-\eta)}. \tag{6.4}$$

It follows, therefore, that the derivative of the left side of (3.23) with respect to either r^R or f^{RS} is $2/V$ times

$$\sum_A \left(4\pi a^2 \delta_{AR} + \frac{4\pi a^3}{3} \frac{4\pi a^2}{V(1-\eta)} \right) \left\{ (-a + 4\pi a^2 G_A) \left(r^A + \sum_{B \neq A} f^{AB} + \tfrac{1}{3} a K^* \right) + 4\pi a^2 \sum_{B \neq A} G_{AB} \left(r^B + \sum_{C \neq B} f^{BC} + \frac{a}{3} K^* \right) \right\} - \frac{a^2(5-\eta)}{15(1-\eta)} K^* + \frac{\bar{c}}{1-\eta}, \tag{6.5}$$

whose conditional expectation keeping x_R fixed gives the variation with respect to r^R, while the variation with respect to f^{RS} is obtained by keeping x_R and x_S fixed. Again, as in § 5, great simplification is achieved if conditional expectations of mean values are replaced directly by their unconditional expectation values. Then, if we define

$$\phi_R = (-a + 4\pi a^2 G_R) \left(r^R + \frac{a}{3} \langle K^* \rangle + \int P_{B|R} f^{RB} \, \mathrm{d}x_B \right) + 4\pi a^2 \int P_{B|R} G_{RB} \left(r^B + f^{BR} + \frac{a}{3} \langle K^* \rangle \right) \mathrm{d}x_B + 4\pi a^2 \times \iint P_{BC|R} G_{RB} f^{BC} \, \mathrm{d}x_B \, \mathrm{d}x_C \tag{6.6}$$

and

$$\psi_{RS} = (-a + 4\pi a^2 G_R)\left(r^R + \frac{a}{3}\langle K^*\rangle + f^{RS} + \int f^{RB} P_{B|R}\,\mathrm{d}x_B\right)$$
$$+ 4\pi a^2 G_{RS}\left(r^S + \frac{a}{3}\langle K^*\rangle + f^{SR} + \int f^{SC} P_{C|RS}\,\mathrm{d}x_C\right)$$
$$+ 4\pi a^2 \int G_{RB}\left(r^B + \frac{a}{3}\langle K^*\rangle + f^{RB} + f^{BS}\right) P_{B|RS}\,\mathrm{d}x_B$$
$$+ 4\pi a^2 \iint G_{RB} f^{BC} P_{BC|RS}\,\mathrm{d}x_B\,\mathrm{d}x_C, \tag{6.7}$$

considering the variation with respect to r^R gives

$$\phi_R + \frac{4\pi a^3}{3}\frac{1}{V(1-\eta)}\int \phi_A P_A\,\mathrm{d}x_A - \frac{a^2(5-\eta)\langle K^*\rangle}{15(1-\eta)} + \frac{\bar{c}}{1-\eta} = 0 \tag{6.8}$$

while considering the variation with respect to f^{RS} gives

$$\psi_{RS} + \frac{4\pi a^3}{3}\frac{1}{V(1-\eta)}\int P_A \phi_A\,\mathrm{d}x_A - \frac{a^2(5-\eta)\langle K^*\rangle}{15(1-\eta)} + \frac{\bar{c}}{1-\eta} = 0. \tag{6.9}$$

Equation (6.8) has exactly the form of (5.4) and it follows that the new ϕ_R still satisfies (5.5). Equation (6.9) now implies that

$$\psi_{RS} = \phi_R = \tfrac{1}{15}a^2(5-\eta)\langle K^*\rangle - \bar{c}, \tag{6.10}$$

so that both are independent of their arguments. Analogously to (5.6), we now set

$$r^A + \int f^{AB} P_{B|A}\,\mathrm{d}x_B = \frac{(1-\eta)}{3\eta}\,a\langle K^*\rangle + \mathrm{e}^A, \tag{6.11}$$

so that e^A still satisfies (5.7). The equation for ϕ_R gives, after rearrangement,

$$(-a + 4\pi a^2 G_R)\{(a/3\eta)\langle K^*\rangle + \mathrm{e}^R\}$$
$$+ 4\pi a^2 \int G_{RB}[\{(a/3\eta)\langle K^*\rangle + \mathrm{e}^B\}(P_{B|R} - P_B) + f^{RB} P_{B|R}]\,\mathrm{d}x_B$$
$$+ 4\pi a^2 \iint G_{RB} f^{BC}(P_{BC|R} - P_{B|R}P_{C|B})\,\mathrm{d}x_B\,\mathrm{d}x_C$$
$$+ 4\pi a^2 \int G_{RB}[(a/3\eta)\langle K^*\rangle(P_B - n) + \mathrm{e}^B P_B]\,\mathrm{d}x_B - \tfrac{1}{15}a^2(5-\eta)\langle K^*\rangle + \bar{c} = 0. \tag{6.12}$$

If V is taken large and it is assumed that $f^{BC} \to 0$ as $|x_B - x_C| \to \infty$ and that the voids have no long-range order, it follows, as in § 5, that e^B is small except in a boundary layer close to ∂V and finally we conclude that, except when x_R is close to ∂V,

$$(a^2/3\eta)\langle K^*\rangle\left\{1-4\pi a\int G_{RB}(P_{B|R}-P_B)\,\mathrm{d}x_B+\tfrac{1}{5}\eta(5-\eta)\right\}$$
$$-4\pi a^2\int G_{RB}f^{RB}P_{B|R}\,\mathrm{d}x_B-4\pi a^2\iint G_{RB}f^{BC}(P_{BC|R}-P_{B|R}P_{C|B})\,\mathrm{d}x_B\,\mathrm{d}x_C=\bar{c}. \tag{6.13}$$

The integrals involving f converge so long as f^{RB} tends to zero appropriately as $|x_B - x_R|$ tends to infinity. The other deduction from (6.10) is that $\psi_{RS} - \phi_S = 0$. Explicitly, when x_R and x_S are not close to ∂V, this reduces to

$$-a\left(f^{RS}+\int f^{RB}(P_{B|RS}-P_{B|R})\mathrm{d}x_B\right)$$
$$+4\pi a^2 G_{RS}\left\{(a/3\eta)\langle K^*\rangle+f^{SR}+\int f^{SC}(P_{C|RS}-P_{C|S})\,\mathrm{d}x_C\right\}$$
$$+4\pi a^2\int G_{RB}[\{(a/3\eta)\langle K^*\rangle+f^{BR}\}(P_{B|RS}-P_{B|R})+f^{BS}P_{B|RS}]\,\mathrm{d}x_B$$
$$+4\pi a^2\iint G_{RB}f^{BC}(P_{BC|RS}-P_{BC|R}-P_{B|RS}P_{C|B}+P_{B|R}P_{C|B})\,\mathrm{d}x_B\,\mathrm{d}x_C=0. \tag{6.14}$$

Equation (6.14), although of some theoretical interest, is of little practical use because it involves correlations of up to four voids which will be unknown in practice. It is, however, possible to obtain an approximate solution valid at low concentrations of voids, by retaining only terms of zeroth order in the number density n. This eliminates the double integral, and also terms involving $P_{B|RS} - P_{B|R}$, since such integrands are 'short-range' and the integrals converge with no assistance from f itself. The one integral that does not have this feature is retained, however, to give

$$-af^{RS}+4\pi a^2 G_{RS}f^{SR}+(4\pi a^3/3\eta)\langle K^*\rangle G_{RS}+4\pi a^2\int G_{RB}f^{BS}P_B\,\mathrm{d}x_B\sim 0, \tag{6.15}$$

the error committed by replacing $P_{B|RS}$ by P_B being of order n. When $|x_R - x_S| \gg a$, the term $4\pi a^2 G_{RS}f^{SR}$ may be dropped and then, taking the Laplacian of (6.15), it follows that

$$-a\nabla^2 f^{RS}+4\pi a^2 n f^{RS}=-(4\pi a^3/3\eta)\langle K^*\rangle\delta(x_R-x_S), \tag{6.16}$$

since $P_B \sim n$. The right side of (6.16) is, of course, only a formal approximation. Equation (6.16) has the solution

$$f^{RS}=-\frac{a^2}{3}\langle K^*\rangle\frac{\exp(-\beta|x_R-x_S|)}{|x_R-x_S|}, \tag{6.17}$$

where

$$\beta^2 = 4\pi a n. \tag{6.18}$$

This analysis, although approximate, demonstrates that an exponential decay is predicted for f^{RS}. An approximate correction to the bound given by equation (5.13) may be obtained by substituting (6.17) back into (6.13) and neglecting the double integral. This gives

$$(a^2/3\eta)\langle K^*\rangle\left\{1+\int\frac{(P_{B|R}-P_B)}{|x_B-x_R|}\,\mathrm{d}x_B - a^2\int\frac{\exp(-\beta|x_B-x_R|)}{|x_B-x_R|^2}P_{B|R}\,\mathrm{d}x_B + \tfrac{1}{5}\eta(5-\eta)\right\} = \bar{c}, \tag{6.19}$$

though the estimate supplied by (6.19) is no longer necessarily a bound.

7. Perturbation theory

In the limit $\eta \ll 1$, it is possible to obtain a solution of the integral equation (3.7) (with (3.8)) in the form of a perturbation series. The problem has not been studied previously in this formulation but the outline to follow is closely related to work of Brailsford (1976) on the diffusion problem and work of Hinch (1977) on problems for viscous fluids. In each case, the methods of solution are variants of one proposed by Lax (1952) in the context of scattering problems.

Equation (3.7) may be written explicitly in the form

$$\int_{\partial V_A} G(x, x')\,q^A(x)\,\mathrm{d}s + \left\{\sum_{B\neq A}\left[\int_{\partial V_B} G(x, x')\,q^B(x)\,\mathrm{d}s + K^*\int_{V_B} G(x, x')\,\mathrm{d}x\right] - K^*\int_{V-V_A} G(x, x')\,\mathrm{d}x\right\} + \bar{c} = 0, \quad x'\in\partial V_A, \quad A = 1, 2, \ldots, N, \tag{7.1}$$

in which q^A denotes the restriction of q to ∂V_A. K* satisfies (3.16) but, assuming statistical uniformity, K^* is identified with its expectation value $\langle K^*\rangle$. Taking the expectation of equation (7.1), conditional upon the void A being fixed, now gives

$$\int_{\partial V_A} G(x, x')\,q_A^A(x)\,\mathrm{d}s + \int_{V-V_A}\left\{\left[\int_{\partial V_B} G(x, x')\,q_{AB}^B(x)\,\mathrm{d}s + \langle K^*\rangle\int_{V_B} G(x, x')\,\mathrm{d}x\right]P_{B|A} - \langle K^*\rangle G(x_B, x')\right\}\mathrm{d}x_B + \bar{c} = 0, \quad x'\in\partial V_A, \tag{7.2}$$

in which $q_A^A(x)$ denotes the expectation value of $q^A(x)$, conditional upon x_A being fixed, and $q_{AB}^B(x)$ denotes the expectation of $q^B(x)$, conditional upon x_A and x_B being fixed. Now at low concentrations of voids, few voids will be close together and it is reasonable to postulate that

$$q_{AB}^B(x) \sim q_B^B(x), \tag{7.3}$$

with an error that is serious only for the few voids that are close. The approximation (7.3) is identical in form to the 'quasicrystalline approximation' of Lax (1952). If it

is accepted as an identity, equation (7.2) becomes an integral equation for $q_A^A(x)$ which yields, in fact, precisely the equation (5.13) for $\langle K^* \rangle$. Thus, although the above reasoning strictly justifies retention only of the lowest-order terms in (5.13), it is interesting to note that (7.3), if taken literally, in fact yields a lower bound for $\langle K^* \rangle$. A similar observation for the 'overall modulus' problem has been made by Willis (1979).

A better approximation may be obtained, essentially following Hinch (1977) and Brailsford (1976), by generating an equation for $q_{AB}^A(x)$ from the expectation of equation (7.1) conditional upon x_A and x_B being fixed. This produces an equation rather like (7.2), except that it involves also $q_{ABC}^C(x)$. An appropriate closure assumption, analogous to (7.3), is that

$$q_{ABC}^C(x) \sim q_{AC}^C(x) + q_{BC}^C(x) - q_C^C(x); \tag{7.5}$$

this is seriously in error only when all three voids are close. Following through the details, retaining only the two terms of lowest order, this time yields a result that is consistent with (6.19).

Under the assumptions of Section 5, it emerged that q^A was constant except close to ∂V, so that $q^A \approx q_A^A$. Also, because q^A was independent of the position of other voids, the quasicrystalline approximation (7.3) was realized exactly. In § 6, however, it emerged that r^A was constant and f^{AB} was translation-invariant. If these conclusions are accepted. it follows that

$$q_{ABC}^C = q_{AC}^C + q_{BC}^C - q_C^C + \int f^{CD} [P_{D|ABC} - P_{D|AC} - P_{D|BC} + P_{D|C}] \, \mathrm{d}x_D, \tag{7.6}$$

in which the integrand is significant only when the voids A, B and C are close, since the medium has no long-range order. It is therefore, not a total surprise that (7.3) generates (5.13) exactly while (7.5) is consistent with a two-term expansion of (6.19). It should be noted, however, that perturbation theory of this type makes heavy demands upon physical intuition in disregarding boundary layer terms that a more careful analysis shows are in some initial danger of dominating the solution, coming, as they do, from integrals that could become unbounded as V becomes indefinitely large.

8. Results and discussion

The main results of this work are the bound $\langle K^* \rangle$ for $\langle K' \rangle$ contained in equation (5.13) and the low-concentration approximation given by (6.19). It is convenient to express the results in terms of the mean normalized flux F into each void:

$$F = n^{-1} \langle K' \rangle (1-\eta)/\bar{c} = (4\pi a^3/3\eta\bar{c})(1-\eta)\langle K' \rangle. \tag{8.1}$$

Equations (5.13) and (6.19) are also simplified by setting

$$P_A = n \tag{8.2}$$

and

$$P_{B|A} = ng(x), \tag{8.3}$$

where

$$x = |x_B - x_A|/2a. \tag{8.4}$$

Performing the trivial angular integration now gives, from (5.13), the lower bound

$$F_1 = 4\pi a(1-\eta)\left[1-5\eta-\tfrac{1}{5}\eta^2+12\eta\int_1^\infty (g(x)-1)\,x\,dx\right]^{-1} \tag{8.5}$$

and, from (6.19), the estimate

$$F_2 \doteq 4\pi a(1-\eta)\left[1-5\eta-\tfrac{1}{5}\eta^2+12\eta\int_1^\infty (g(x)-1)\,x\,dx - 6\eta\int_1^\infty \exp\left(-2(3\eta)^{\frac{1}{2}}x\right) g(x)\,dx\right]^{-1}. \tag{8.6}$$

The latter is valid only at small values of η and so could equally well be expanded suitable powers of η.

Before we proceed further, it may be remarked that the restriction to a fixed number N of voids may be relaxed, by regarding the expectations so far derived as being conditional upon N and then taking expectations over N, the mean number density n now being interpreted as $\langle N\rangle/V$.

The pair distribution function $g(x)$ is zero for $0 \leqslant x < 1$, since the voids are not allowed to overlap, and tends to 1 as x tends to infinity. It must, in fact, also satisfy some other restrictions if it is to be the result of any stochastic mixing process. Although a complete set of restrictions is unknown, this remark may be illustrated by considering for the moment the 'well-stirred approximation' defined by

$$g(x) = 1, \quad 1 < x < \infty, \tag{8.7}$$

which has been used in the low-concentration limit by Batchelor & Green (1972) and Willis & Acton (1976), for example, and at arbitrary concentrations by Varadan *et al.* (1978) in different physical contexts. When (8.7) is substituted into (8.5), the integral disappears and it is seen that the lower bound F_1 becomes infinite at a value of η just less than 0.2. Since F_1 was obtained from the expectation value of a functional that plainly remains finite, it must concluded that the well-stirred approximation (8.7) is untenable at concentrations around or above 0.2. At very high concentrations, it is plausible that $g(x)$ at least should rise above 1 when x is close to 1, since knowledge that a sphere is centred at a given point must almost guarantee the presence of spheres close to $x = 1$ when the spheres are rather tightly packed. The integral in the denominor of (8.5) is then likely to be positive and should ensure that F_1 remains finite.

In view of the sensitivity of F_1 (and also F_2) to the form of $g(x)$, we abandon the study of abstractions such as (8.7) and instead substitute some genuinely plausible forms for $g(x)$. The first two are rigorously attainable, having been derived by Matérn (1960) from explicitly defined stochastic models. The simpler of Matérn's models is obtained by sampling a Poisson process of intensity α and deleting any point which is within $2a$ of any other, whether or not this has already been deleted. For this model,

$$\eta = v\alpha\,e^{-8v\alpha}, \tag{8.8}$$

where $v = \frac{4}{3}\pi a^2$, and

$$g(x) = \exp[v\alpha(16-\phi(x))], \quad 1 \leqslant x < \infty, \tag{8.9}$$

where

$$\left.\begin{aligned} \phi(x) &= 8+6x-\tfrac{1}{2}x^3, \quad 0 \leqslant x \leqslant 2 \\ &= 16, \quad 2 \leqslant x < \infty. \end{aligned}\right\} \tag{8.10}$$

so that $v\phi(x)$ represents the volume of the region occupied by two spheres, each of radius $2a$, whose centres are $2ax$ apart. It may be noted that $g(x) = 1$ for $x \geqslant 2$, while $g(x) > 1$ for $1 \leqslant x < 2$, taking its maximum value $\exp(\frac{27}{2}v\alpha)$ at $x = 1$. Thus, the model displays some 'piling up' of probability around $x = 1$, even at low concentrations. The model is limited, however, in allowing only low concentrations, the maximum value of η being approximately 0.046, attained when $v\alpha = 1/8$.

In Matérn's second model, the points of a Poisson process of intensity α are independently marked with a uniformly distributed birth time on (0, 1) so that they are, in effect, generated from a Poisson process on $R^3 \times (0, 1)$. Any given point is retained if no point within $2a$ has an earlier birth time. With the slightly unnatural inclusion of points already deleted in applying this criterion, Matérn was able to show that

$$\eta = \tfrac{1}{8}(1-e^{-8v\alpha}) \tag{8.11}$$

and

$$g(x) = \frac{16\phi(x)(1-e^{-8v\alpha}) - 128(1-e^{-v\alpha\phi(x)})}{\phi(x)(\phi(x)-8)(1-e^{-8v\alpha})^2}, \quad 1 \leqslant x < \infty. \tag{8.12}$$

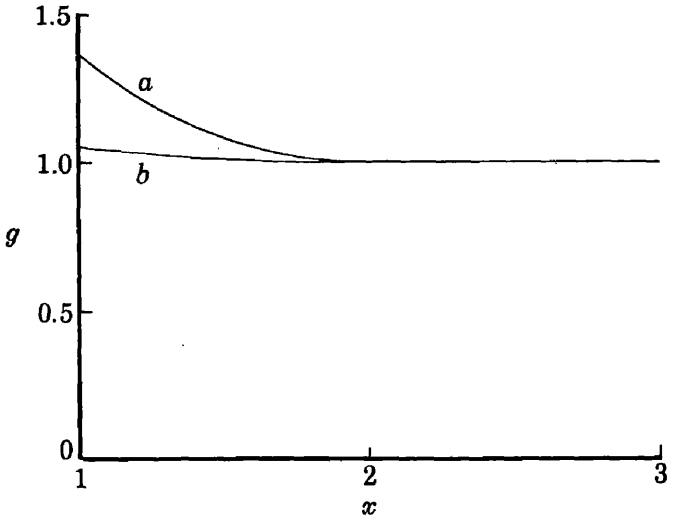


FIGURE 1. Plots of the pair distribution function $g(x)$, at volume density $\eta = 0.046$, for the two Matérn models: (*a*) given by equation (8.9) and (*b*) given by equation (8.12).

Again, $g(x) = 1$ when $x \geqslant 2$ and $g(x)$ is greatest at $x = 1$. The range of concentrations is not as limited as in Matérn's first model, but still $\eta \leqslant 1/8$. The functions $g(x)$ corresponding to each of Matérns' models are graphed in figure 1, for $\eta = 0.046$, the limit of validity of the first. Plots of the bounds F_1, and of the estimates F_2, are displayed in figure 2. At low concentrations ($v\alpha \to 0$), both of Matérn's models reduce

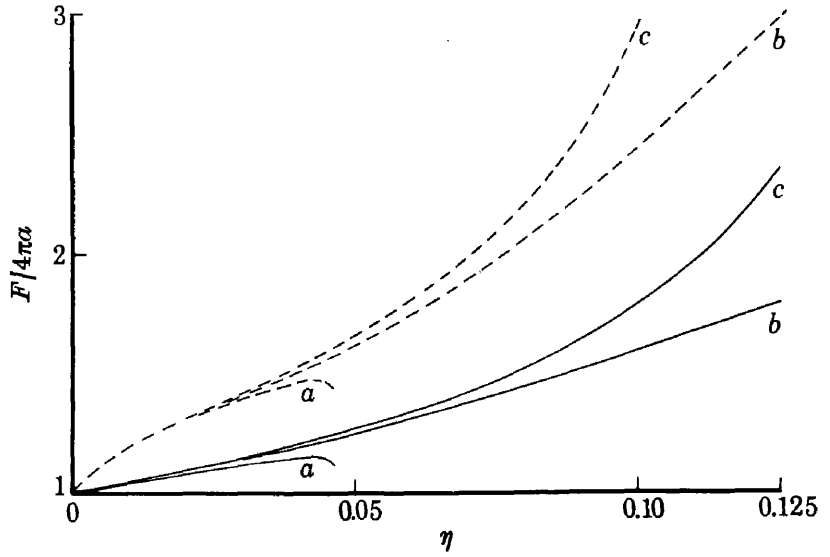


FIGURE 2. Plots of lower bound estimates F_1 (continuous lines) and low-concentration approximations F_2 (dashed lines) for the two Matérn models (a) and (b) and for the well-stirred approximation (c).

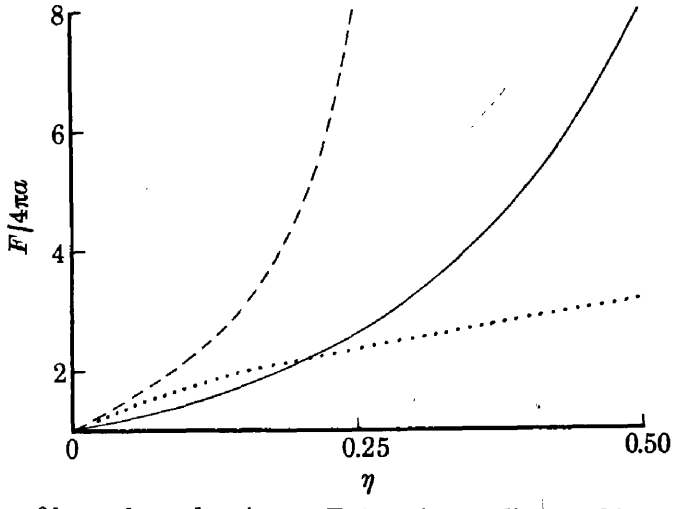


FIGURE 3. Plots of lower bound estimate F_1 (continuous line) and low-concentration approximation F_2 (dashed line) for the Percus–Yevick model. The dotted line shows the self-consistent approximation.

to the well-stirred approximation (8.7) and F_1 and F_2 associated with this approximation are also shown. Each model gives as $\eta \to 0$,

$$F_2 \sim 4\pi a(1+(3\eta)^{\frac{1}{2}}), \tag{8.13}$$

which is precisely consistent, to this order, with the self-consistent approximation generated from (2.13).

In the absence of any precisely realisable $g(x)$ valid at arbitrary concentrations, plots of F_1 and F_2 associated with the Percus–Yevick hard-sphere approximation are given in figure 3. Percus & Yevick (1957) generated an integral equation that $g(x)$ should approximately satisfy by treating a statistical mechanical system of hard spheres, with one sphere in a fixed position, as a perturbation of the system

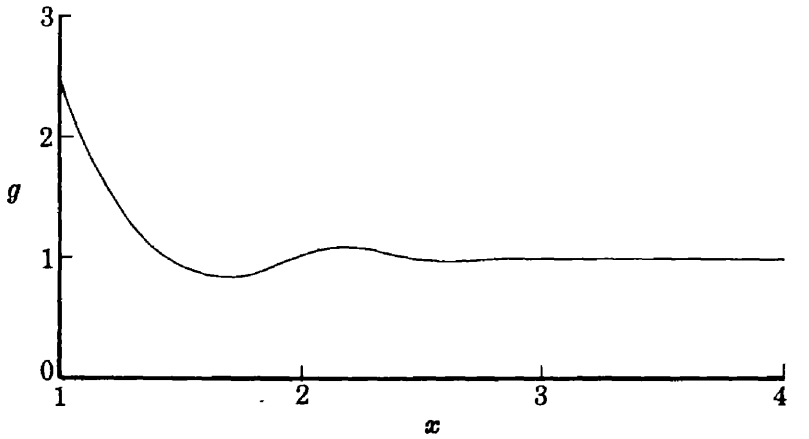


FIGURE 4. The Percus–Yevick pair distribution function $g(x)$ at volume density $\eta = \frac{1}{10}\pi$.

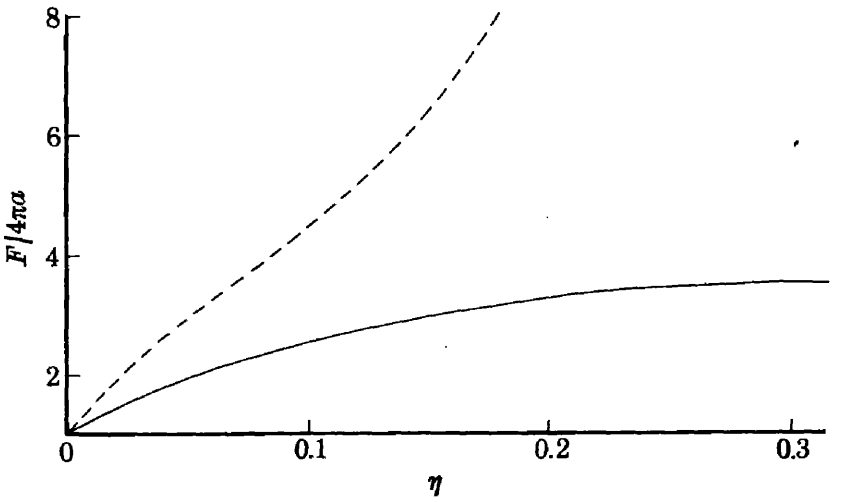


FIGURE 5. The lower bound and low-concentration approximation for the well separated model.

with that particular sphere absent. The Percus–Yevick integral equation was solved by Wertheim (1963) who found the Laplace transform of $xg(x)$ in closed form, and $g(x)$ has been tabulated by Throop & Bearman (1964). A typical plot of $g(x)$, taken from this tabulation, with $\eta = \frac{1}{10}\pi$ so that $8na^3 = 0.6$, is shown in figure 4. It is a fortunate coincidence that the integral in the bound (8.5) contains the integral of $xg(x)$ and so can be obtained analytically from the small argument asymptotic behaviour of the Laplace transform. The result, obtained with the aid of Wertheim's expression, is

$$\int_1^\infty (g(x)-1)x\,\mathrm{d}x = \tfrac{1}{2} - \frac{(\frac{1}{2}\alpha+\frac{1}{3}\beta+\frac{1}{5}\delta)+4\eta(\frac{1}{5}\alpha+\frac{1}{6}\beta+\frac{1}{8}\delta)}{1+24\eta(\frac{1}{3}\alpha+\frac{1}{4}\beta+\frac{1}{6}\delta)} \tag{8.14}$$

where

$$\alpha = \frac{(1+2\eta)^2}{(1-\eta)^4}, \quad \beta = -\frac{6\eta(1+\eta/2)^2}{(1-\eta)^4}, \quad \delta = \frac{\eta(1+2\eta)^2}{2(1-\eta)^4}. \tag{8.15}$$

For values of η up to about 0.3, the result (8.14) agrees well with a numerical evaluation obtained from the tabulation of Throop & Bearman (1964), but

thereafter the oscillating tail that remains for $x > 4$, the limit of the tabulation, is significant. The estimate F_2, obtained from equation (8.6), contains a further integral that has to be evaluated numerically. The plot of F_2 against η displays a singularity for η around 0.27, showing that the perturbation has well and truly broken down by this stage. However, at lower values of η, say up to 0.1, which is probably around the limit of validity of the approximation, the effect of replacing $g(x)$ by 1 in fact is small, so that a fair analytic approximation to F_2 can be generated throughout its range of usefulness.

Also displayed on figure 3 is a plot of F as calculated from the self-consistent equation (2.13). It follows the approximation F_2 at low concentrations but actually lies below the lower bound F_1 when η is greater than 0.2, approximately. Exactly what distribution it approximates, if any, at higher concentrations, is uncertain.

Finally, a distribution of 'well-separated' type has been constructed in which centres of spheres are separated by at least $2kn^{-\frac{1}{3}}$. A distribution with this property could be realized in statistical mechanics by making the interaction energy between a pair of spheres infinite if their centres are separated by less than $2kn^{-\frac{1}{3}}$. Thus, they behave rather like spheres of radius $a' = kn^{-\frac{1}{3}}$ and a pileup of probability is to be expected around their minimum separation. If x is now defined as $|x_B - x_A|/2a'$ it follows that $P_{B|A}$ is given by (8.3), where $g(x)$ is the pair distribution function corresponding to spheres of radius a' at number density n. F_1 and F_2 then take the forms

$$F_1 = 4\pi a(1-\eta)\left[1+\eta-\tfrac{1}{5}\eta^2-6\eta^{\frac{1}{3}}(\tfrac{4}{3}\pi)^{\frac{2}{3}}k^2+12(\tfrac{4}{3}\pi)^{\frac{2}{3}}k^2\eta^{\frac{1}{3}}\int_1^\infty (g(x)-1)x\,\mathrm{d}x\right]^{-1} \tag{8.16}$$

$$F_2 = 4\pi a(1-\eta)\left[1+\eta-\tfrac{1}{5}\eta^2-6\eta^{\frac{1}{3}}(\tfrac{4}{3}\pi)^{\frac{2}{3}}k^2+12(\tfrac{4}{3}\pi)^{\frac{2}{3}}k^2\eta^{\frac{1}{3}}\int_1^\infty (g(x)-1)x\,\mathrm{d}x - 6\eta^{\frac{2}{3}}(\tfrac{4}{3}\pi)^{\frac{1}{3}}k\int_1^\infty \exp[-2\sqrt{3}(\tfrac{4}{3}\pi)^{\frac{1}{3}}k\eta^{\frac{1}{6}}x]\,g(x)\,\mathrm{d}x\right]^{-1}. \tag{8.17}$$

The possible validity of this approximation is limited by the requirement that $a' \geqslant a$, from which it follows that

$$\eta \leqslant \tfrac{4}{3}\pi k^3. \tag{8.18}$$

The concentration $\eta' = 4\pi n a'^3/3$ from which $g(x)$ is calculated remains constant at $\frac{4}{3}\pi k^3$, and, for realizability, this must be less than the density for maximimum packing. This is given by Hansen & McDonald (1976) as $\pi/3\sqrt{2}$ and a concentration around 0.5 is considered to be close to crystallization.

It is interesting to note that, as $\eta \to 0$, (8.16) yields

$$F_1 \sim 4\pi a\left[1+6(\tfrac{4}{3}\pi)^{\frac{2}{3}}k^2\eta^{\frac{1}{3}}\left(1-2\int_1^\infty (g(x)-1)\,x\,\mathrm{d}x\right)\right]. \tag{8.19}$$

This lies above both the bound F_1 and the estimate F_2 obtained from the well-stirred approximation, which all of our earlier models approach in this limit. Plots

of the bound (8.16) and the estimate (8.17) are displayed in figure 5, for $g(x)$ as in the Percus–Yevick approximation, with k chosen as 0.4217. This corresponds to $8na^3 = 0.6$, or $\eta' = \frac{1}{10}\pi$, for which $g(x)$ is shown in figure 3. The values of F_1 and F_2 coincide with those obtained from the 'ordinary' Percus–Yevick approximation when $\eta = \eta'$ as they should, and are greater than the corresponding 'ordinary' values when $\eta < \eta'$.

In conclusion, we note the sensitivity of the sink strength to the precise distribution of the voids. In practice, pair distribuion functions will be unknown and then the simple self-consistent estimate seems a natural choice: it is adequate at low void densities and could be modified to allow for a well-separated distribution by placing a sink-free region adjacent to the void considered explicitly. At higher void densities, however, the self-consistent estimate may be in error and use of the bound (8.5) seems preferable, even with the pair distribution function $g(x)$ estimated in some approximate way. For other problems involving a variety of competing sink types, similar remarks might be expected to apply: the evidence of the present study suggests that self-consistent estimates provide a reasonable first approximation, but that estimates based upon making closure assumptions like (7.3), which are rigorously valid only at low concentrations, but then making no further approximation, are likely to yield better results at high sink concentrations.

One of us (D. R. S. T.) gratefully acknowledges the support of the Science Research Council and the Atomic Energy Research Establishment, Harwell, through the tenure of an S.R.C. C.A.S.E. studentship. Thanks are due to Professor R. Sibson (University of Bath) and Dr R. Bullough and Dr M. J. Gillan (A.E.R.E. Harwell) for helpful discussions.

References

Batchelor, G. K. & Green, J. T. 1972 *J. Fluid Mech.* **56**, 401.
Bensoussan, A., Lions, J. L. & Papanicolaou, G. 1978 *Asymptotic analysis for periodic structures*. Amsterdam: North-Holland.
Brailsford, A. D. 1976 *J. nucl. Mat.* **60**, 257.
Brinkman, H. C. 1974 *Appl. Sci. Res* A **1**, 27.
Bullough, R. & Hayns, M. R. 1978 Continuum Models of Discrete Systems. *Proc. Int. Conf.*, Mont Gabriel, Quebec, June 1977, p. 469. University of Waterloo Press.
Childress, S. 1972 *J. Chem. Phys.* **56**, 2527.
Hansen, J. P. & McDonald, I. R. 1976 *Theory of simple liquids*. London: Academic Press.
Hashin, Z. & Shtrikman, S. 1962*a* *J. Mech. Phys. Solids* **10**, 335.
Hashin, Z. & Shtrikman, S. 1962*b* *J. Mech. Phys. Solids* **10**, 343.
Hashin, Z. & Shtrikman, S. 1963 *J. Mech. Phys. Solids* **11**, 127.
Hayns, M. R. & Bullough, R. 1975 *Thermodynamics of nuclear materials*, vol. I. *Proc. Int. Conf.*, Vienna, 1974, I.A.E.A.-S.M.-190/15, p. 217.
Hill, R. 1952 *Proc. Phys. Soc.* A **65**, 349.
Hinch, E. J. 1977 *J. Fluid Mech.* **83**, 659.
Howells, I. D. 1974 *J. Fluid Mech.* **64**, 449.
Korringa, J. 1973 *J. math. Phys.* **14**, 509.
Kröner, E. 1977 *J. Mech. Phys. Solids* **25**, 137.
Lax, M. 1952 *Phys. Rev.* **85**, 621.

Matérn, B. 1960 *Meddn St. SkogsforskInst.* **49**, 5, 7.
Percus, J. K. & Yevick, G. J. 1957 *Phys. Rev.* **110**, 1.
Throop, G. J. & Bearman, R. J. 1964 *J. Chem. Phys.* **42**, 2408.
Varadan, V. K., Varadan, V. V. & Pao, Y.-H. 1978 *J. Acoust. Soc. Am.* **63**, 1310.
Wertheim, M. S. 1963 *Phys. Rev. Lett.* **10**, 321.
Willis, J. R. & Acton, J. R. 1976 *Q. Jl. Mech. appl. Math.* **29**, 163.
Willis, J. R. 1977 *J. Mech. Phys. Solids* **25**, 185.
Willis, J. R. 1978 Continuum Models of Discrete Systems. *Proc. Int. Conf., Mont Gabriel, Quebec, June* 1977, p. 185. University of Waterloo Press.
Willis, J. R. 1979 Variational Methods in Mechanics of Solids. *Proc. Int. Conf., Northwestern University*, September 1978. Pergamon Press.